Technical Report
TR-2288-ENV

ESTIMATING CLEANUP TIMES ASSOCIATED WITH COMBINING SOURCE-AREA REMEDIATION WITH MONITORED NATURAL ATTENUATION

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February 2008

REPORT DOCUMENTATION PAGE		*Form Approved* *OMB No. 0704-0811*

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1. REPORT DATE *(DD-MM-YYYY)* 12-FEBRUARY-2008	2. REPORT TYPE Technical Report	3. DATES COVERED *(From – To)* 14-August-2008 to 12 February-2008

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
ESTIMATING CLEANUP TIMES ASSOCIATED WITH COMBINING SOURCE-AREA REMEDIATION WITH MONITORED NATURAL ATTENUATION	N47408-04-C-7524
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Mark Widdowson, Phd, PE, Virginia Tech **Francis Chapelle, Phd, United States Geological Survey** **Clifton Casey, PE, NAVFAC SOUTH** **Mark Kram, Phd, NAVFAC ESC**	ESTCP ER-0436
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESSES	8. PERFORMING ORGANIZATION REPORT NUMBER
Naval Facilities Engineering Service Center **1100 23rd Avenue** **Port Hueneme, CA 93043**	**TR-2288-ENV**

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITORS ACRONYM(S)
Environmental Security Technology Certification Program **901 North Stuart Street, Suite 303** **Arlington, VA 22203**	ESTCP
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
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In response, the Natural Attenuation Software (NAS) was co-developed by the Naval Facilities Engineering Command (NAVFAC), U.S. Geological Survey (USGS), and Virginia Tech. NAS is a screening tool designed for estimating time of remediation (TOR) for MNA with varying degrees of source area remediation. Conventional screening tools for MNA are not designed to address source zone remediation options or simulation of plume reduction. The NAS consists of a combination of computational tools implemented in three main interactive modules to provide estimates for: 1) target source concentration required for a plume extent to contract to regulatory limits, 2) time required for contaminants in the source area to attenuate to a predetermined target source concentration, and 3) time required for a plume extent to contract to regulatory limits after source reduction. Natural attenuation processes that NAS models include are advection, dispersion, sorption, non-aqueous phase liquid (NAPL) dissolution, and biodegradation of petroleum hydrocarbons, chlorinated solvents, or any user-specified contaminants or mixtures. NAS can also be used to determine the equilibrium concentrate at any given location following source-zone remediation and when this will occur.

15. SUBJECT TERMS

NAS, MNA, TOR, source area, source-zone, NAPL, DNAPL, LNAPL, remediation, groundwater

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Mark Kram
U	U	U		192	19b. TELEPHONE NUMBER *(include area code)* 805-982-2669

ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM

FINAL TECHNICAL REPORT

FOR

ESTIMATING CLEANUP TIMES ASSOCIATED WITH COMBINING SOURCE-AREA REMEDIATION WITH MONITORED NATURAL ATTENUATION

February, 2008

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ACRONYMS

ADEC	Alaska Department of Environmental Conservation
ADOT&PF	Alaska Department of Transportation and Public Facilities
AFB	Air Force Base
ARAR	applicable or relevant and appropriate requirements
BGS	below ground surface
BRAC	Base Realignment and Closures
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CVOC	chlorinated volatile organic compound
DCE	Dichloroethene
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DOS	distance of plume stabilization
ERA	engineered remedial action
ESTCP	Environmental Security Technology Certification Program
FDEP	Florida Department of Environmental Protection
MCAS	Marine Corps Air Station
MCL	maximum contaminant level
MCLG	maximum contaminant level goals
MNA	Monitored Natural Attenuation
NAES	Naval Air Engineering Station
NAPL	non-aqueous phase liquid
NAS	Natural Attenuation Software
NASCF	Naval Air Station Cecil Field
NAVFAC	Naval Facilities Engineering Command
NCP	National Contingency Plan
NPL	National Priority List
NSB	Naval Submarine Base

ORC	oxygen release compound
OU	Operational Unit
PCB	polychlorinated biphenyl
PCE	tetrachloroethene
RI/FS	Remedial Investigation/Feasibility Study
RITS	Remediation Innovative Technology Seminar
RFI	RCRA Facility Investigation
ROD	Record of Decision
RPM	remedial project manager
SDWA	Safe Drinking Water Act
SEAM3D	Sequential Electron Acceptor Model, 3D transport
SEDA	Seneca Army Depot Activity
SI	surface impoundment
SVOC	semi-volatile organic compounds
TCA	trichloroethane
TCE	trichloroethene
TEAP	terminal electron acceptor processes
TND	time of NAPL dissolution
TOR	time of remediation
TOS	time of plume stabilization
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VC	vinyl chloride
VOC	volatile organic compound
WWTP	waste-water treatment plant

ACKNOWLEDGEMENTS

EXECUTIVE SUMMARY

Under suitable conditions, monitored natural attenuation (MNA) can be a cost-effective strategy for restoring contaminated aquifer systems either as a stand-alone technology or in combination with other engineered remedial actions. However, USEPA guidance specifically requires MNA to achieve site-specific cleanup objectives within a reasonable time frame. Thus, it is necessary to provide estimates of cleanup times whenever MNA is proposed as part of a cleanup strategy.

In response, the Natural Attenuation Software (NAS) was co-developed by the Naval Facilities Engineering Command (NAVFAC), U.S. Geological Survey (USGS), and Virginia Tech. NAS is a screening tool designed for estimating time of remediation (TOR) for MNA with varying degrees of source area remediation. Conventional screening tools for MNA are not designed to address source zone remediation options or simulation of plume reduction. The NAS consists of a combination of computational tools implemented in three main interactive modules to provide estimates for: 1) target source concentration required for a plume extent to contract to regulatory limits, 2) time required for contaminants in the source area to attenuate to a predetermined target source concentration, and 3) time required for a plume extent to contract to regulatory limits after source reduction. Natural attenuation processes that NAS models include are advection, dispersion, sorption, non-aqueous phase liquid (NAPL) dissolution, and biodegradation of petroleum hydrocarbons, chlorinated solvents, or any user-specified contaminants or mixtures. NAS can also be used to determine the equilibrium concentrate at any given location following source-zone remediation and when this will occur.

The objective of this demonstration was to evaluate the NAS software capability to provide reasonable estimates of MNA cleanup timeframes in a variety of environments and sites throughout the United States. The tool is evaluated by using data from eight sites with long-term monitoring data that encompass diverse geologic and hydrogeochemical environments and various engineered remedial actions (ERA). Results were judged based on accuracy, versatility, reliability, and applicability. The objective of the project was to validate NAS using a consistent set of procedures for comparing predicted and observed TOR results. Sites were selected to represent a range of different hydrologic settings and ERAs. The eight demonstration sites are located at Seneca Army Depot and a USGS study site in New York, NAES Lakehurst in New Jersey, Hill AFB in Utah, NSB Kings Bay in Georgia, Naval Air Station Cecil Field and Naval Air Station Pensacola in Florida and a USGS study site in Alaska.

The distance/time of stabilization (DOS/TOS) feature of NAS was tested at 5 sites and the time of NAPL dissolution (TND) feature was tested at the remaining 3 test sites. Overall, the DOS/TOS feature was satisfactory in meeting quantitative and qualitative performance objectives based on the match between NAS and the data inflection points and concentration versus time slopes, respectively. NAS was effective in predicting the time of stabilization of concentrations at monitoring wells located relatively close to the source (up to 700 ft downgradient) following source remediation and a subsequent reduction in groundwater contaminant concentrations in the source zone. Factors affecting the degree of accuracy were reflected in the uncertainty associated with the contaminant velocity estimates and source characteristics (width and concentration) following remediation. The TND feature was

satisfactory in meeting the qualitative performance objective associated with source zones. NAS was effective in capturing concentration time trends of natural source depletion of a multi-component NAPL, providing a prediction that was superior to a comprehensive numerical model that was not based on source zone mass balance.

One finding of this demonstration was that NAS proved to be applicable to all eight sites, independent of hydrogeology, contaminants, characteristics of the source zone, or ERA. Therefore, the simplifying assumptions associated with the analytical solutions and the numerical source zone model do not appear to render NAS ineffective but, in fact, demonstrate the applicability and utility of NAS to a wide range of contaminated sites. In contrast, comprehensive three-dimensional numerical models that are constructed to simulate the complexities of a groundwater system and features of a plume often are subject to limited data and may include unrealistic boundary conditions that do not honor the actual field conditions. However, there are many sites where complex hydrogeology, highly non-uniform groundwater flow, and the desire to simulate complicated remediation strategies will dictate the use of a comprehensive numerical model.

NAS, a methodology and tool for estimating the time of remediation associated with MNA, will allow stakeholders to make informed decisions regarding its application. In addition, budget requirements for long term monitoring programs can be forecasted based on estimates of timeframes. This allows better program planning to meet the future needs of cleanup programs, and can afford remedial project managers (RPM) the ability to conduct cost benefit analyses when comparing source removal with MNA options to MNA-only strategies. The estimated cost of implementing NAS was compared to cost estimates using a comprehensive numerical model at a site to address the TOR question. The estimated cost of implementing a comprehensive numerical model was 5.6 times greater than the estimated cost of using NAS. It is reasonable to assume that this ratio will be even greater when overhead and costs associated with oversight by senior technical experts and regulating agencies are included.

1. Introduction

1.1. Background

Monitored Natural Attenuation (MNA) is a remedial alternative recognized by the United States Environmental Protection Agency (USEPA) that relies on naturally occurring processes to achieve site-specific remediation objectives within a time frame that is reasonable when compared to other alternatives (USEPA 1999). The cleanup timeframe is defined as a period of time during which the quality of ground-water will achieve a certain level at a specific location (USEPA 2001). A precursor, therefore to selection of MNA as a viable remedy requires a quantitative estimate of the time to reach remediation objectives. Estimating the cleanup time associated with MNA requires evaluation of a variety of physical, chemical and biological attenuation mechanisms. To estimate cleanup timeframes based on these processes, a screening level tool is needed that can be used by project scientists and engineers to make informed decisions during remedy selection.

At sites where simplifying assumptions related to ground-water flow and transport can be made, a computational model can be used to estimate the behavior of plumes and source zones where MNA is being considered. The Naval Facilities Engineering Command (NAVFAC), Southern Division, partnered with the United States Geological Survey (USGS, South Carolina District) and Virginia Polytechnic Institute and State University (Virginia Tech) to develop a screening level modeling tool to estimate the site-specific cleanup time for MNA. The result of that collaboration was the development of the Natural Attenuation Software (NAS) funded by NAVFAC. This tool was designed to evaluate plume dynamics such as the projected plume length, the time for the plume to stabilize, the time required for the plume to attenuate as well as estimates of the cleanup timeframes following an engineered remedial application (ERA) to remove the contaminant source, including non-aqueous phase liquids (NAPL). When used in conjunction with ERAs of source zones, MNA may be considered as a part of a combined remedy. Under these circumstances, NAS can be used to establish nonzero cleanup thresholds for actively engineered remedies in the source area that will meet time, distance and exposure constraints of the project. Although NAS had been previously applied to data from several field sites, there is a need to demonstrate and validate this enhanced NAS approach by comparing model predictions to field observations from sites representing a wide-range of conditions.

1.2. Objectives of the Demonstration

The objective of this demonstration is to evaluate the capability of the NAS software to provide reasonable estimates of MNA cleanup timeframes in a variety of environments and sites throughout the United States. The tool is evaluated by using data from eight sites with long-term monitoring data that encompass diverse geologic and hydrogeochemical environments and different remediation options. An evaluation of predictions from early data sets with empirical

data during the predicted period is used to make assessments of the utility of the estimates. Table 1 lists the scope and locations of the demonstrations.

Table 1. Locations of Demonstrations

Facility	Site	Location	Contaminant(s)
Seneca Army Depot	Ash Landfill	Romulus, NY	Chlorinated ethenes
Textron	USGS Site	Niagara Falls, NY	Chlorinated ethenes
NAES Lakehurst	Sites I & J	Lakehurst, NY	Chlorinated ethenes
Hill Air Force Base	OU2	Ogden, UT	Chlorinated ethenes
Naval Submarine Base Kings Bay	Site 11	Kings Bay, GA	Chlorinated ethenes
Naval Air Station Cecil Field	Site 3	Jacksonville, FL	Chlorinated ethenes and chlorinated benzenes
Naval Air Station Pensacola	WWTP	Pensacola, FL	Chlorinated ethenes and chlorinated benzenes
ADOT&PF	USGS Site	Fairbanks, AK	Chlorinated ethenes

1.3.   Regulatory Drivers

Remedial actions at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites must be protective of human health and the environment and comply with applicable or relevant and appropriate requirements (ARAR). Drinking water standards provide relevant and appropriate cleanup levels for ground-waters that are a current or potential source of drinking water. Drinking water standards include federal maximum contaminant levels (MCL) and/or non-zero maximum contaminant level goals (MCLG) established under the Safe Drinking Water Act (SDWA), or more stringent state drinking water standards. Selection of MNA as a remedy for cleanup of hazardous substances requires that estimates of time of cleanup be made to assess its feasibility as a remedy.

1.4.   Stakeholder Issues

Stakeholder buy-in is evident by the support provided by Navy Engineering Field Divisions. This is exemplified by the recently funded NAS upgrade to allow for incorporation of a source removal term. Earlier versions of NAS have been the subject of Navy supported conference presentations (e.g., the annual RPM Conference) and a RITS course module. End-user concerns, reservations, and buy-in factors all point to the remedial project managers' (RPM) willingness to utilize the NAS approach versus a more comprehensive modeling effort. Concerns with implementation have been addressed through the NAS site applications using feedback from users during this demonstration.

2. Technology Description

2.1. Technology Description and Application

Overview of Monitored Natural Attenuation

Monitored natural attenuation is the considered use of naturally occurring contaminant degradation/dispersion/immobilization processes to reach site-specific remediation goals (USEPA 1996; 1998). In current engineering practice, the effectiveness of MNA is evaluated on a site-by-site basis by considering three lines of evidence: (1) historical monitoring data showing decreasing concentrations and/or contaminant mass over time, (2) geochemical data showing that site conditions favor contaminant transformation or immobilization, or (3) site-specific laboratory studies documenting ongoing biodegradation processes (USEPA 1998). A variety of field and laboratory methods for assessing these three lines of evidence have been developed and are currently in use (Wiedemeier et al. 1999).

More recently, it has been pointed out that these "lines of evidence" reflect the more general principle of mass balance (USDOE 2003). If, for example, the capacity of a ground-water system to attenuate contaminants exceeds the mass loading of contaminants to that system, then the efficiency of MNA is considered relatively high (Line of evidence #1). Conversely, if the delivery of contaminants exceeds this natural attenuation capacity, then the efficiency of MNA is proportionally lower. In either case, this contaminant loading/attenuation balance is affected by ambient geochemical conditions (Line of evidence #2) and can be assessed by laboratory studies as well as field studies (Line of evidence #3). The successful implementation of MNA requires a quantitative assessment of how contaminant mass loading is balanced by the natural attenuation capacity of a given system relative to site-specific remediation objectives.

Time of Remediation Associated with Natural Attenuation

In concept, estimating the length of time required for natural processes to remove a particular contaminant from a ground-water system is a simple mass balance problem. If the initial mass of contaminant, M_o, (units of mass) present in a ground-water system is known, and if the rate that the contaminant is transformed or destroyed by natural attenuation processes, R_{NA}, (units of mass removed per unit time) is known, a mass balance equation can be written

$$M(t) = M_o - \int_0^t R_{NA} \, dt \tag{1}$$

in which t is time and $M(t)$ is the contaminant mass remaining at any time t. It follows that a time of remediation can be defined as the time required to lower contaminant mass below a given threshold (M^*):

$$M^* = M_o - \int_0^{t^*} R_{NA} \, dt \tag{2}$$

where the t^* is time of remediation (TOR) is defined explicitly as given in Equation (2), and refers to the length of time needed for a given mass of initial contaminant (M_o) to be lowered below a given regulatory threshold (M^*), by the rate of natural attenuation processes (R_{NA}) occurring in a ground-water system.

In addition to providing a working definition of TOR, Equation (2) also indicates the kinds of information necessary to make remediation time estimates. This information includes an estimate of the mass of contaminant present, and an estimate of the rate of ongoing natural attenuation processes acting on the contaminant. The principal technical problem, therefore, is to obtain reliable estimates of these parameters. Clearly, the reliability of any remediation time estimates will be directly linked to the reliability of the parameter estimates. In addition, Equation (2) shows that determining remediation times requires the definition of an acceptable contaminant mass threshold. This threshold must be predetermined in order to make remediation time estimates.

In practice, however, the problem is much more complex than indicated by Equation (2), primarily because the term R_{NA} is the sum of several processes that include advection, hydrodynamic dispersion, biodegradation, and dissolution from NAPL or diffused/sorbed contaminant sources. Widdowson (2004) expressed the mass balance equation of an aqueous-phase constituent in the form:

$$-v_i \frac{\partial C_l}{\partial x_i} + \frac{\partial}{\partial x}\left(D_{ij} \frac{\partial C_l}{\partial x_j} \right) + \frac{q_s}{\theta} C_l^* - R_{sink,l}^{bio} + R_{source,l}^{bio} + R_{source,l}^{NAPL} = R_l \frac{\partial C_l}{\partial t} \tag{3}$$

where C_l is the aqueous phase contaminant concentration [M L^{-3}]; x_i is distance [L]; t is time [T]; v_i is the average linear ground-water velocity [L T^{-1}]; D_{ij} is the tensor for the hydrodynamic dispersion coefficient [L^2 T^{-1}]; C_l^* is the contaminant point source concentration [M L^{-3}]; q_s is the volumetric flux of water per unit volume of aquifer [T^{-1}]; θ is the effective porosity [L^o]; R_l is the contaminant retardation factor [L^o]; $R_{sink,l}^{bio}$ is a biodegradation mass loss term dependent on the mode of respiration [M L^{-3} T^{-1}]; $R_{source,l}^{bio}$ is a source term for the biogenic mass production [M L^{-3} T^{-1}]; $R_{source,l}^{NAPL}$ is a source term due to NAPL dissolution [M L^{-3} T^{-1}].

The NAPL source term for petroleum hydrocarbons and chlorinated compounds utilizes first-order kinetics for dissolution from a multiple-component mixture

$$R_{source,lc}^{NAPL} = k^{NAPL}\left(C_l^{eq} - C_l \right) \tag{4}$$

where k^{NAPL} is the NAPL dissolution rate constant [T^{-1}]; and C_l^{eq} is the equilibrium contaminant concentration [M L^{-3}], represented as the product of the solubility of the constituent in water and the mole fraction, f_l, of NAPL constituent l. The mole fraction is a function of the mass fractions of the NAPL constituents

$$f_l = \frac{C_l^{NAPL} / \omega_l}{I^{NAPL} / \omega_I + \sum_{l=1}^{NS} C_l^{NAPL} / \omega_l} \tag{5}$$

where C_l^{NAPL} is the NAPL mass of constituent l per unit mass dry soil [M M_{solid}^{-1}]; and ω_l is the molecular weight of NAPL constituent l; and I^{NAPL} is the NAPL concentration of the inert (i.e., relatively insoluble) fraction [M M_{solid}^{-1}];. The mass balance equation for the NAPL phase is expressed as

$$\frac{dC_i^{NAPL}}{dt} = -\frac{\theta}{\rho_b} R_{source,i}^{NAPL} \tag{6}$$

where ρ_b is the bulk density of the porous medium [M_{solid} L^{-3}]

For the multicomponent NAPL problems, solutions to quantify TOR using Equations (3) through (6) are achieved using numerical models. SEAM3D (Sequential Electron Acceptor Model, 3D transport) is a code designed to simulate the transport and attenuation of contaminants subject to aerobic and anaerobic biotransformations (Waddill and Widdowson 2000). SEAM3D includes mass balance equations for a multi-component NAPL. The rate of release for each NAPL constituent is a function of mass transport and transfer parameters (v_i and k^{NAPL}), NAPL parameters (mass, mole fraction and geometry), and chemical properties (molecular weight and solubility) of the NAPL components.

Using solutions to Equation (3), Chapelle et al. (2003) divided the time of remediation problem into three parts: 1) distance of plume stabilization (DOS), 2) time of plume stabilization (TOS), and 3) time of NAPL dissolution (TND). Each of these issues can be addressed using particular solutions of Equation (3), which can be developed according to specific needs. NAS was developed to make use of solutions to Equation (3) in order to address these three classes of TOR problems. This software was designed to aid the user in assembling and organizing the data needed to make TOR estimates, to obtain appropriate and useful solutions of the TOR equation, and to illustrate the various uncertainties inherent in TOR estimates. No attempt has been made to make NAS applicable to all, or even most, TOR problems. Rather, NAS is designed around numerous simplifications of hydrologic, microbial, and geochemical processes that, while convenient, may introduce unacceptable error to some problems. The NAS software can be downloaded from the website http://www.nas.cee.vt.edu/.

Overview of NAS Software

The NAS tool is designed for application to ground-water systems consisting of porous, relatively homogeneous, saturated media such as sands and gravels. In its present form NAS is not intended for simulating solute transport in dual-domain porous media such as fractured rock aquifers and highly heterogeneous unconsolidated aquifers. Version 1 of NAS was designed specifically for petroleum hydrocarbon and chlorinated ethene contaminants. Version 2 was recently updated for an expanded range of contaminant groups and to provide greater flexibility for adding additional contaminants and groups.

First, detailed site information about hydrogeology, redox conditions, and contaminant concentrations must be entered. Table 2 provides a summary of the required site data. The goal of site data assessment is to determine site-specific, contaminant-specific degradation rates using an inverse modeling technique. NAS is primarily designed as a screening tool early in the RI/FS process following completion of a site investigation and characterization. If the data NAS requires is not available, then TOR estimates can not and should not be made. However, another use of NAS is to reveal site data deficiencies that can be addressed during the RI/FS process and to develop monitoring strategies.

Table 2. Summary of NAS v2.2 Site Data Requirements

Hydrogeology
Hydraulic conductivity[1]
Hydraulic gradient[1]
Fraction of organic matter[1]
Total Porosity[2]
Effective Porosity[2]
Average saturated thickness impacted by contamination[2]
Redox[3]
Dissolved oxygen (DO), Ferrous iron, Sulfate
Optional: Nitrate, Mn(II), Sulfide, Methane, Dissolved hydrogen
Contaminant[3]
Chlorinated Ethenes: PCE (*optional*), TCE, and daughter products
Petroleum Hydrocarbons: Benzene, Toluene, Ethylbenzene, Xylene, MTBE (*optional*), Naphthalene (*optional*)
Chlorinated Ethanes: TCA and daughter products
Chlorinated Methanes: carbon tetrachloride and daughter products
Requirements
[1]Best estimate, maximum, minimum
[2]Best estimate
[3]Values from 3 or more wells along the solute plume flow path

Figure 1 shows a flowchart describing how the NAS software can be used to address time of remediation questions. After data entry, NAS estimates site-specific ground-water flow rates, biodegradation rates, and sorption properties. Based on the range of estimates, NAS then produces either analytical or numerical solutions of the TOR equation. As shown in Fig. 1, one option employs analytical solutions to determine the target reduction in the source area concentration to meet site-specific remediation goals. This approach and solution addresses plume concentration questions, such as what is the distance to which a plume will re-stabilize for given source-area contaminant concentrations, and how long will it take to see the desired effects at a down-gradient point of compliance. For the DOS question, NAS calculates the allowable maximum source-area concentration, based on a regulatory maximum concentration level at a given point downgradient of the source. Then, NAS estimates how long it will take for the

plume to reach the lower steady-state configuration once source-area concentrations have been lowered by engineering methods. Once both the DOS and the TOS are acceptable, based on site-specific regulatory criteria, MNA can become an integral component of site remediation (Fig. 1).
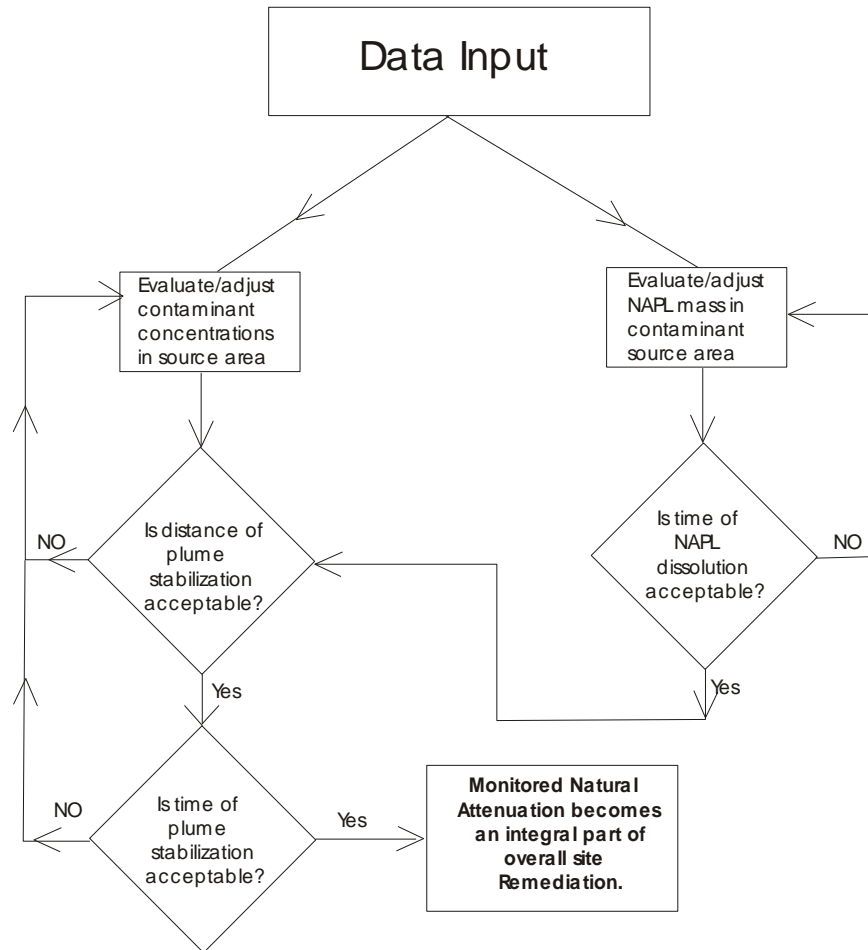
Figure 1. Flowchart showing how the NAS software can be applied to TOR problems.

The other option is a source zone mass-balance approach to determine the target reduction in the source zone NAPL or residual contaminant mass to reduce the TOR based on site-specific remediation goals. To achieve this solution, NAS uses the SEAM3D code (Waddill and Widdowson 1998) to solve Equations (3) through (6) in conjunction with a ground-water flow code (MODFLOW). The solution provided by NAS is tailored to estimate the length of time required by a given NAPL mass to dissolve and lower contaminant concentrations at the source area below a given user-supplied threshold.

In principle, the numerical solution could then be used to estimate the distance and time of stabilization for the remaining residual concentration. Since this would significantly lengthen the amount of time required to complete a simulation, numerical simulation is not presently practical for DOS and TOS problems. Rather, once the target source zone concentration is

determined by an analytical solution and the numerical solution is completed (time required to reach this target calculation), the analytical solution for the time of stabilization can be implemented (Fig. 1). Thus, the estimated total TOR to reach compliance at a distance downgradient of the source (e.g., plume toe) is the sum of the two solutions.

2.2. Previous Testing of the Technology

Prior application of NAS has been documented in Chapelle et al. (2003) using limited data sets from two sites: NSB Kings Bay, GA (chlorinated ethenes) and MCAS Beaufort, SC (petroleum hydrocarbons). Although these two sites have different contaminant plumes, they share two key characteristics: (1) high-quality, long-term ground-water monitoring data and (2) long-term decline in contaminant concentrations in source-area monitoring wells following source remediation. Mendez et al. (2004) presented the application of NAS at the MCAS Beaufort, SC to simulate the depletion of benzene concentrations at a source-area monitoring well based on estimates of ground-water velocity and LNAPL mass, composition, and dimensions.

2.3. Factors Affecting Cost and Performance

Factors affecting cost and performance of MNA include time of remediation, effectiveness of source remediation technology, number of monitoring wells and frequency of sampling events, and sustainability of NA processes. The remediation timeframe, discussed above, will most directly control the cost of MNA performance monitoring. Source-control ERAs that involve the removal of mass (residual contaminants and/or NAPL) are instrumental in MNA strategies to decrease plume length and decrease the remediation timeframe. Lastly, MNA, particularly biological NA processes, must be sustainable over the remediation timeframe. Project costs will increase if aggressive remedial strategies are required to stimulate microbial transformations (e.g., vegetable oil).

Costs associated with implementing NAS include data assembly and execution of NAS. Based on past experience, the latter requires only 1-2 hours per data set. Data requirements for NAS are consistent with the Department of Defense (DoD) protocols for MNA, and additional data required when using numerical models are not necessary when using NAS. In effect, the application of NAS at sites provides value-added to performance monitoring programs.

2.4. Advantages and Limitations of the Technology

NAS offers several advantages relative to comprehensive ground-water modeling of sites. Even when NAS estimates TOR using the SEAM3D NAPL Dissolution Package, the user is not required to specify numerical parameters (e.g., grid spacing) or any spatial input parameters. Because NAS includes a simple self-calibrating analytical model, the amount of time and effort required is much less a site model for ground-water flow and solute transport. However, at the

sites with complex hydrogeology and patterns of ground-water flow comprehensive ground-water modeling offers greater capabilities relative to NAS. While hydrogeology and flow patterns obviously play a large role, an accurate and complete characterization of the source area is essential to effective remediation of the source zone (NRC 2004). Likewise, any mathematical model may not be accurate if the source term is estimated based on limited information. Modeling tools, including NAS, are useful in developing and refining site conceptual models of the aqueous plume and source zones and in exposing site characterization deficiencies.

In comparison to conventional engineered remediation technologies, MNA offers a number of advantages (http://www.afcee.brooks.af.mil):

1. During intrinsic bioremediation, contaminants can be ultimately transformed to innocuous byproducts (e.g., carbon dioxide, ethene, chloride, and water in the case of chlorinated solvents; and carbon dioxide and water in the case of fuel hydrocarbons), not just transferred to another phase or location within the environment;

2. MNA is minimally intrusive and allows continuing use of infrastructure during remediation;

3. Except for assessment and monitoring efforts, natural attenuation does not involve generation or transfer of waste;

4. MNA is often less costly than other currently available remediation technologies;

5. MNA can be used in conjunction with, or as a follow-up to, other intrusive remedial measures;

6. MNA is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime).

MNA has the following potential limitations:

1. Time frames for complete remediation may be long;

2. Responsibility must be assumed for long-term monitoring and its associated cost, and the implementation of institutional controls;

3. Natural attenuation is subject to natural and anthropogenic changes in local hydrogeologic conditions, including changes in ground-water flow direction or velocity, electron acceptor and donor concentrations, and potential future releases;

4. The hydrologic and geochemical conditions amenable to MNA are likely to change over time and could result in renewed mobility of previously stabilized contaminants (e.g., manganese and arsenic) and may adversely impact remedial effectiveness;

5. Aquifer heterogeneity may complicate site characterization, as it will with any remedial approach; and

6. Intermediate products of biodegradation (e.g., vinyl chloride, VC) can be more toxic than the original compound (e.g., trichloroethene, TCE).

3. Demonstration Design

3.1. Performance Objectives

The objective of the demonstration is to assess the performance of NAS as a computational tool for estimating remediation timeframes following source zone remediation. To achieve this objective, NAS will be implemented to simulate contaminant concentrations at chlorinated solvents sites that represent a range of conditions. NAS is designed to first calibrate an analytical solution to steady-state plume contaminant concentration data and to then implement analytical and numerical solutions to simulate the transient response of plume concentrations due to source-zone treatment, depletion, or some combination of the above. In this demonstration, NAS was primarily implemented in the predictive mode, allowing for an assessment of the accuracy of TOR estimates.

Results of the application of NAS to sites at NSB Kings Bay, GA and MCAS Beaufort, SC (Figures 2 and 3) suggest several metrics that can be used to post audit TOR estimates:

1. Predicted/measured *inflection points* of contaminant concentration profiles.
2. Predicted *time of breakthrough*.
3. Predicted/measured *slopes* of contaminant concentration profiles.
4. Predicted/measured contaminant concentration profiles for different NAPL components over time.

The first three metrics (*inflection points, time of breakthrough,* and *slopes* of contaminant concentration profiles) are demonstrated in Fig. 2, which depicts total chlorinated ethene concentration changes at a location downgradient of the source following treatment. Point (A1) represents the time at which the impact of source remediation is observed at a downgradient monitoring well. This point of inflection is identified at the time where a consistent decline of contaminant concentration is observed. The second inflection point (A2) corresponds to the time required to reach a new steady-state concentration at a specific location within the solute plume. The point (B) corresponds to the time of breakthrough where 50% of the net decrease in concentration is observed. The slope (C) is the rate of decline in the concentration between points A1 and A2.

The fourth metric listed (concentration decline in individual NAPL components) is reflected in Fig. 3. The benzene concentration decline (data shown) was observed to occur at an accelerated rate relative to the other BTEX (toluene, ethylbenzene, and xylene) compounds (Mendez et al. 2004). This metric is relevant at sites with multi-component NAPL sources. One example is a combined source of chlorinated solvents and petroleum hydrocarbons (e.g., fire-training pit). The four metrics are summarized in Table 3.
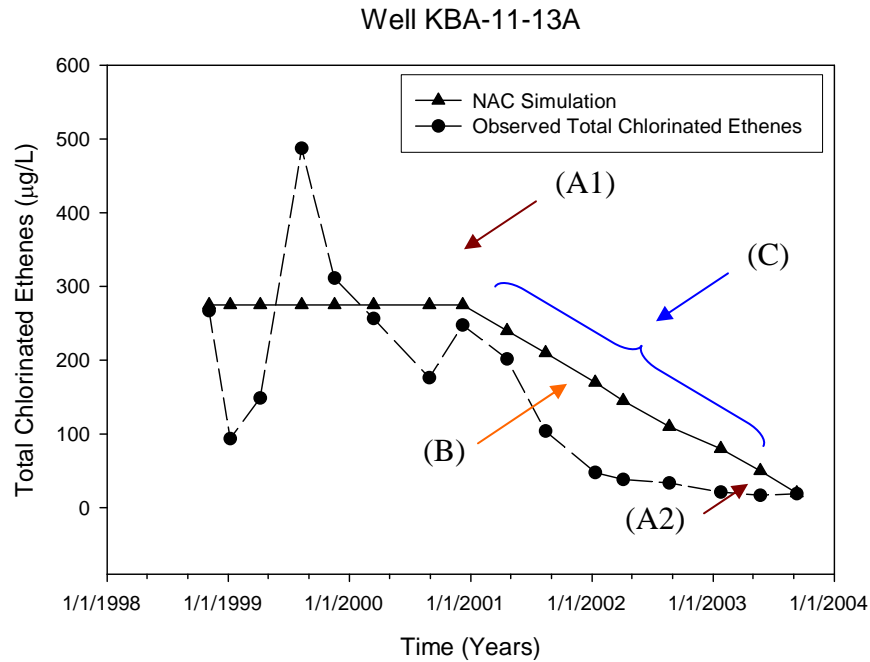
Well KBA-11-13A

Figure 2. Measured versus NAS-simulated concentration changes at well KBA-11-13A. Points (A1) and (A2) are inflection points, (B) is located at the time of breakthrough and (C) indicates the slope of the concentration decline.
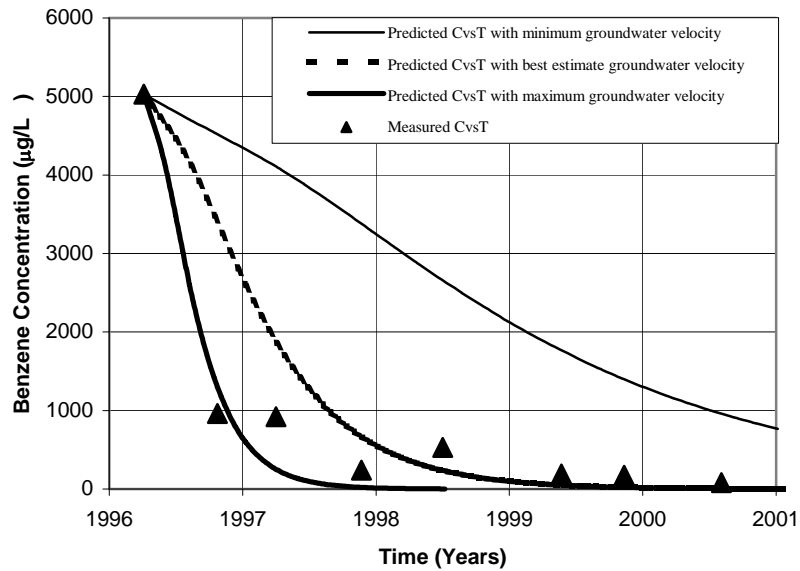
Figure 3. Measured versus NAS-simulated concentration changes at well MW-8.

Table 3. Performance Objectives

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)
Quantitative	Inflection point of concentration-time curve	The predicted inflection point (point A1, Fig. 2) of the concentration-time curve should coincide with the observed inflection point within one year.
Quantitative	Time of breakthrough	The predicted time of breakthrough (point B, Fig. 2) of the concentration-time curve should coincide with the observed breakthrough within two years.
Qualitative	Slope of concentration-time curve following inflection point	The predicted slope of the inflection point of the concentration-time curve (slope C, Fig. 2) should be similar to the observed slope.
Qualitative	Predicted/Observed contaminant-concentration profiles for different components of NAPL	NAS will be assessed for how accurately it predicts that the more soluble NAPL components are removed sooner than the less soluble components.

3.2. Selection of Test Sites

Extensive verification testing of NAS was performed using data from sites with (1) differing hydrogeologic conditions and (2) various methods of source remediation. The criteria and requirements for site selection reflect these two needs. In addition, sites were screened to eliminate sites that do not include (1) high-quality data sets and (2) long-term decline in contaminant ground-water concentrations following source remediation.

Although NAS is ideally suited for sites that have wells near the source and along the center line of the plume coupled with relatively simple hydrogeologic conditions, it was viewed as useful to select some sites with non-ideal conditions. The notion was not to set up the demonstration for failure but to test the limits of the software and assess how robust the solutions are in relation to the performance objectives. For example, at some sites the monitoring infrastructure and sample data resulting from characterization efforts were not specifically aimed at demonstrating MNA lines of evidence or lacked the detail for a comprehensive modeling effort. The conceptual models at some sites were not based on a simple homogeneous unconsolidated aquifer as the site data was indicative of more complex hydrogeologic conditions. Therefore, some of the sites selected for the demonstration exhibited a few non-ideal characteristics.

Desired site characteristics included:

- Five years of annual monitoring data that includes both the geochemical and contaminant chemistry, and water levels

- Appropriate geochemical data that allows for assessment of the plume status in an electron acceptor distribution framework

- Ground-water velocities exceeding 5 ft/year

- Darcy flow (i.e., not conduit flow such as Karst)

- Unidirectional ground-water flow fields and boundary conditions that can be reasonably simulated by the analytical code

Site data sets were screened so that sites where contaminant concentrations did not decline were removed from consideration. Specifically, data from the demonstration sites exhibited either natural depletion of source zones over times or a declining trend in contaminant concentration at downgradient wells following a source-area ERA. Allowance was made for noise in the data and/or variation indicative of sampling or other issues that cannot be sufficiently incorporated into the solution.

Candidate sites were screened based on the availability of redox indicator data collected in accordance with EPA/DoD protocols for MNA (USEPA 1998). Ideal sites included annually-collected geochemical data that enabled determination of the predominate terminal electron accepting processes and the spatial distribution of dominating redox conditions using NAS. Minimally, dissolved oxygen (DO), sulfate, and ferrous iron data were necessary. The geochemical data were examined for potential errors associated with sample collection that may have inadvertently altered the chemistry. For example, DO that exceeds the solubility of ground-water in the aquifer may have been aerated during sample collection.

Ground-water velocities and travel times must be sufficient to measure changes over time relative to the period of time for which monitoring data has been collected. Lower contaminant velocities and travel times were acceptable where monitoring data has been accumulated over longer periods of time. Because the software is not designed to handle conduit flow, sites with hydrogeologic conditions that can best be described as complex fractured bedrock and/or Karst with solution channels were not considered.

The local ground-water flow pattern along the length of the contaminant plume should not be significantly impacted by pumping wells or natural sources and sinks. For example, if the site was situated in a ground-water recharge area where ground-water mounding and divergent flow was observed, then the applicability of NAS may be limited depending on the location of the source relative to the recharge mound. Other boundary conditions had to be relatively simple and adequately described by steady state conditions.

3.3. Test Site Description

The eight sites selected for demonstrations (Table 1) are shown (Figure 4) on the map of the United States. A description of each site is provided in Section 3.3 and includes the history of operation, site maps, site hydrogeology, source and plume description, redox conditions, and past and current remediation approaches.

1. Seneca Army Depot, NY
2. USGS Site, NY
3. NAES Lakehurst, NJ
4. Hill AFB, UT

5. NSB Kings Bay, GA
6. NAS Cecil Field, FL
7. NAS Pensacola, FL
8. USGS Site, AK

Figure 4. Location map for eight selected sites. (Ref: www.nationalatlas.gov)

3.3.1. Seneca Army Depot, NY – Ash Landfill

3.3.1.1. History of Operations

The Seneca Army Depot Activity (SEDA) encompasses 10,587 acres and it locates between Seneca and Cayuga Finger lakes, in Romulus, New York. The site was acquired by the U.S. Government in 1941 to store and dispose of military explosives. In 2000, the military mission in this area ceased causing the site to close down. The site (Ash Landfill) is located along the western boundary of the SEDA with an extension of approximately 130 acres. The operation at the Ash landfill was primary focused on eliminating the trash produced at the depot. This task

was achieved by first burning the solid waste using the refuse burning pits (between 1941 and 1974) or using the incinerator building (between 1974 and 1979). The ashes were stored in an incinerator cooling water pond until filled to be later transported to the Ash Landfill. Those items that could not be burned were discarded at a non-combustible fill landfill. The Ash Landfill site was active until May 8, 1979, when a fire destroyed the incinerator building (Parsons 2004).

3.3.1.2. Site Hydrogeology

Two hydrogeological units are present in the Ash Landfill site. The superficial geological deposit is composed of glacial till. This layer is primary composed of clay, with sand and gravel also present in a lower percentage and with variable distribution. This variability in composition results in a broad range of hydraulic conductivities. Within the boundaries of the site, the thickness of this unit does not exceed 20 feet. The second hydrogeological unit is black fissile shale with small interbedded limestone layers. The upper 5 feet of the shale is weathered as a result of erosive processes. Accordingly, the main aquifer of the zone is formed by the glacial till along with this weathered shale unit. The bedrock to this aquifer is the unaffected shale unit, which has an approximate thickness of 500 feet (Parsons 2004).

3.3.1.3. Source and Plume Description

Between 1979 and 1989, several Army agencies conducted ground-water and solid sampling at the Ash Landfill site to investigate the presence of chlorinated volatile organic compounds (CVOCs) in the local aquifer. These studies revealed the presence of an approximately 18-acres chlorinated plume, emanating from the northern western side of the landfill. Contamination due to PAHs and metals (copper, lead, mercury, and zinc) are also affecting the soil and ground-water of the area, but to a lesser extent (Parsons 2004).

Based on data collected in 1999, the longitudinal and transversal extension of the CVOC plume is 1,300 ft and 625 ft, respectively (Figure 5). The vertical migration of the plume is believed to be restricted to the upper till/weathered shale aquifer. Monitoring well data showed the presence of TCE in 33% of the ground-water samples. A similar number was registered for total cis-1,2-dichloroethene (DCE). Conversely, VC was detected only in 7% of the samples.

The monitoring program conducted in the Ash Landfill site revealed that the CVOC source was located within the Ash Landfill. More specifically, the collected concentration data indicates that the source was situated in the area near monitoring well MW-44A. Following investigations, however, suggest that the CVOC plume has it origins in more than one source. This remark arouse after treating the polluted soil near well MW-44A between 1994 and 1995. The concentration of CVOCs at well MW-44A dropped by more than 95 percent. However, other wells, such as PT-18 and MW-29, continued registering significant contaminant levels in the years following the removal action. The existence of an alleged CVOC source near well PT-18A may account for the limited concentration reduction in these wells.

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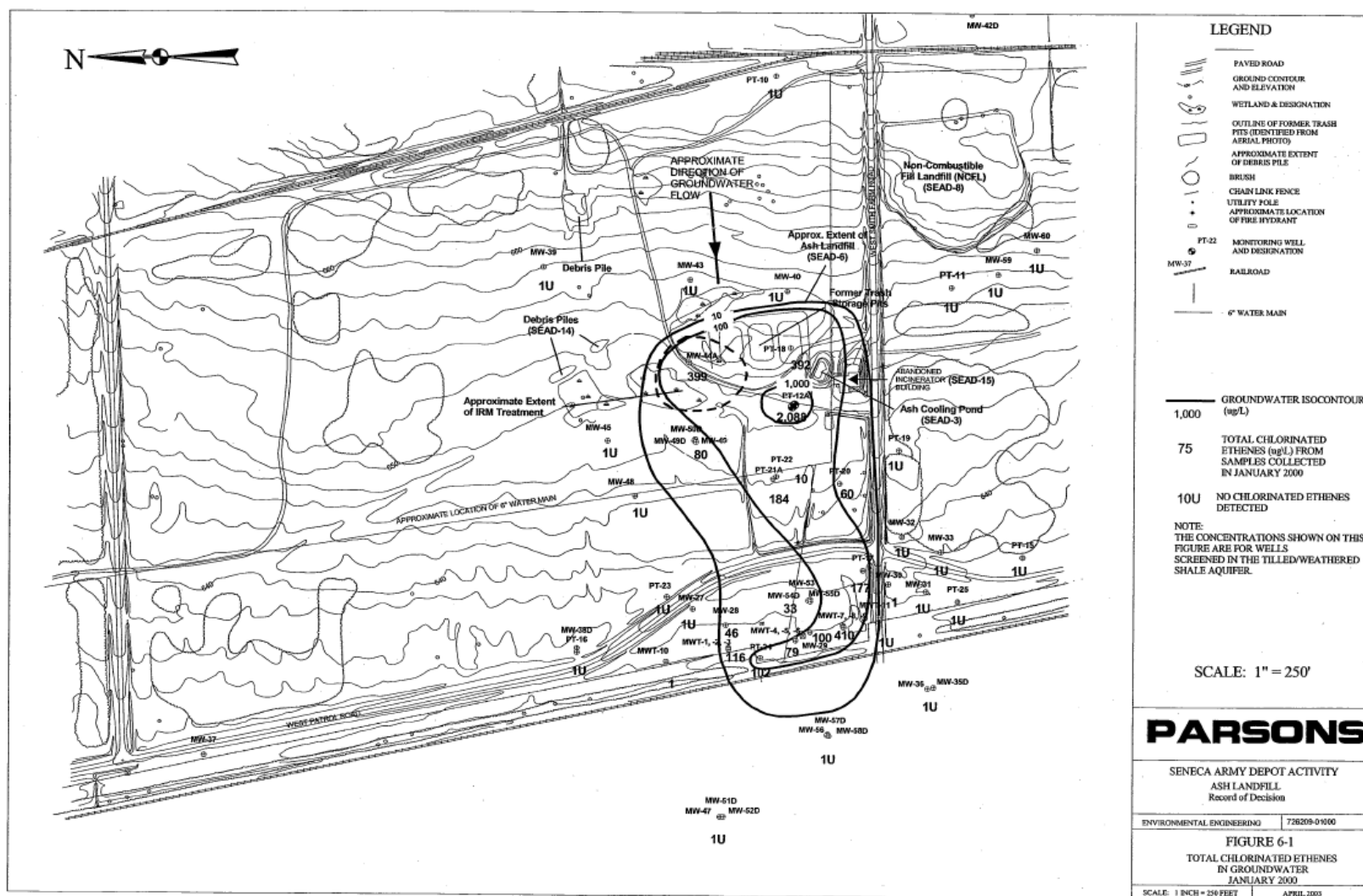
Figure 5. Site map of Ash Landfill at the Seneca Army Depot, NY. (Ref: Parsons Engineering, 2004)

3.3.1.4. Redox Conditions

The redox conditions existing in the aquifer were determined by using the information collected since 1997. This data set is composed of DO, Fe(II), nitrate-nitrite, sulfate, and methane. The aquifer is primarily anaerobic in nature, but high concentrations of sulfate (> 200 mg/L) may mask the exact redox condition. Low levels of Fe(II) and methane and consumption of sulfate along the ground-water flow path suggest that sulfate-reducing conditions are present in the plume. Contaminant data clearly supports that the redox conditions existing in the aquifer promote the reductive dechlorination as the preferential biodegradation process.

3.3.1.5. Past and Current Remediation Approaches

Sampling conducted in the Ash Landfill site revealed that the highest CVOC concentration was registered in well MW-44. This suggested that the contaminant source was located somewhere nearby this well. Accordingly, between 1994 and 1995, a non-time critical removal was performed in this area. The remedial treatment consisted of removing approximately 35,000 tons of soil in this area and heating it to 800-900°F. The treated soil was then used to fill the excavated area. The surface treated area involves approximately 1.5 acres. The benefits of this remedial action have been lately observed as the levels of CVOCs in the ground-water have decreased by more than 95 percent in the treated area.

A 650-foot long permeable reactive iron wall was built in December 1998 with the purpose of controlling the migration of the plume by accelerating reductive chlorination of CVOCs in ground-water. While quality data collected in the wall zone revealed that this permeable wall is quite efficient in removing chlorinated from the aqueous phase, the resulting aqueous concentration levels are still over the maximum level acceptable. A study concluded that better removal rate is to be expected when a longer reactive residence time is imposed. Further prospective remedial alternatives are analyzed and compared in the final Record of Decision (ROD) report prepared by Parsons Engineering in July 2004. The selected remedy is composed of several elements that include excavation and off-site disposal of debris piles and installation of three permeable reactive barrier walls.

3.3.2. Niagara Falls, NY – USGS Site

3.3.2.1. History of Operations

Textron Realty Operations Incorporated (formerly Bell Aerospace Textron) is located at the western end of the Town of Wheatfield, New York. The plant is approximately 2 miles north of the Niagara River and about 3 miles east of US Interstate 190. This former aerospace-defense company conducted research and development, testing, and manufacturing of hardware and navigational and guidance systems (Yager 2002).

The facility's surface impoundment (SI), or neutralization pond, is the only RCRA-regulated unit at the facility, subject to both RCRA post-closure requirements and corrective action. No other RCRA-regulated units were found to be significantly contaminated at the site. The SI was used to collect wash water from rocket engine test firings from 1940 to approximately 1984. It also received storm runoff and cooling water for more than 30 years, and for a limited period, coal gasification wastes. The SI is a rectangular basin, measuring 60 feet by 100 feet by 10 feet, which was closed in 1988 (Yager 2002).

3.3.2.2.   Site Hydrogeology

The study area is adjacent to a manufacturing facility 8 km east of Niagara Falls in western New York (Figure 6). Contaminants from the facility have entered the upper part of the Lockport Group, a 52 m thick dolomite of the Niagaran Series (Middle Silurian) that strikes east-west and dips gently to the south at about 4.6 m/km (Yager 2002). The hydraulic properties of the Lockport Group are related primarily to secondary permeability caused by fractures and vugs. The principal water-bearing zones in the Lockport Group are the weathered bedrock surface and horizontal-fracture zones near stratigraphic contacts. Ground-water flows southward and westward through the Lockport Group from recharge areas near the Niagara Escarpment, 8 km north of the facility, toward discharge areas in low-lying areas near the Niagara River 5 km to the south (Yager 2002).

The manufacturing facility that was the source of TCE overlies 5-12 m of till and lacustrine silt and clay. These unconsolidated deposits are underlain by the upper part of the Lockport Group that has been classified into four zones by previous investigators (Figure 7). Zone 1, which corresponds to the Guelph Formation, is 3-6 m thick and comprises the weathered bedrock layer that contains many open fractures. Zone1 also contains a water-bearing, horizontal-fracture zone near its lower contact with Zone 2, the upper part of the Eramosa Formation. Zone 2 is a massive, 2.4 m thick dolomite that appears relatively unfractured. The TCE remains primarily within Zone 1. The transmissivity of Zone 1 was estimated at 6 m^2/d from a cross-hole pumping test that showed hydraulic connection throughout Zone 1 and no vertical connection between Zones and 1 and 3. Ground-water velocity was computed to range from 0.2-0.9 m/d, from an assumed effective porosity of 3%. (Yager 2002).

3.3.2.3.   Source and Plume Description

VOCs derived from the SI are present in the ground-water as an aqueous (dissolved) phase contaminant plume and as a DNAPL source. Aqueous phase contamination (up to 100,000 parts per million VOCs) has been found in the soils, in the unconsolidated sediments above the bedrock (the overburden) and in the bedrock. The extent of the DNAPL source appears to be limited to the facility property but the extent of the aqueous phase bedrock plume is considerably greater (Figure 6). The plume travels in the upper bedrock aquifer, beneath residential and commercial areas, posing a potential for volatile vapors to migrate from the plume into buildings (USEPA 2004).

Figure 6. Map of USGS study site in Niagara Falls, NY (Ref: Yager 2002).
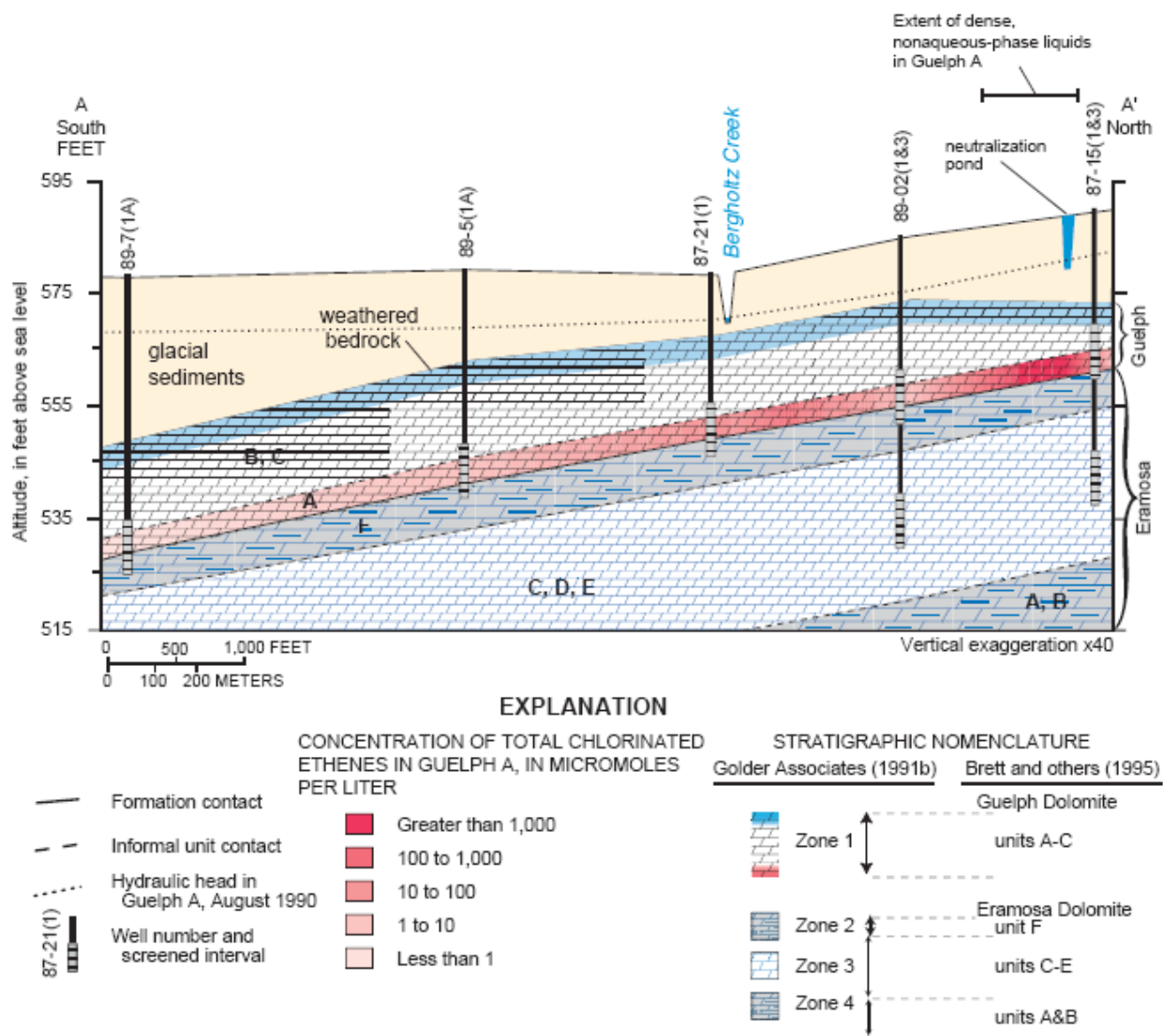
Figure 7. Vertical section A-A' through the chlorinated ethene plume (Ref: Yager 2002).

3.3.2.4. Redox Conditions

Dissolved oxygen concentrations in samples from 23 of 24 wells finished in the Guelph A were less than 0.4 mg/L; and the low concentration measured in the other sample (1.1 mg/L) was probably the result of atmospheric contamination. Hydrogen concentrations in the Guelph A generally range from 0.2 to 0.6 nanomolar (nM), which is indicative of iron-reducing conditions (Chapelle et al. 2004). This conclusion is supported by the presence of ferrous iron (Fe^{2+}) at concentrations above 0.02 mg/L in 17 wells.

3.3.2.5. Past and Current Remediation Approaches

To address the existing contamination and remediate the areas impacted by the contamination, the facility has installed an off-site (5 wells) and an on-site (7 wells) ground-water extraction system. Performance monitoring data indicate that those remedial systems are achieving their design objectives, which are to control the further migration of contaminated ground-water, remove contamination from the ground-water and eventually attain the New York State ground-water standards (EPA 2004). The operation of the off-site and on-site ground-water extraction systems started in 1993 and 1995 respectively. The above-ground source of the contamination has been removed, and the extent of the contaminant plume has diminished. Due to the physical characteristics of the DNAPL, remediation of the source by pumping or other extraction methods is not technically feasible. The effective alternative is to control the dissolution of the DNAPL by hydraulically or physically containing the source (Yager 2002).

3.3.3. NAES Lakehurst, NJ – Sites I&J

3.3.3.1. History of Operations

The Naval Air Engineering Station (NAES) Lakehurst station presents a surface of 7,412 acres and it is located within the Pinelands National Reserve in central New Jersey. Lakehurst began as a remote ammunition proving ground for the Russian Imperial Government in 1915. Currently, Lakehurst operates as the Aircraft Platform Interface Group for technical mission support. Area I, which consists of five contaminants sites, is located in the south central portion of the facility and catapult test facility built in 1958. Area J, which consists of four contaminants sites, is located in the central-western portion of the facility to the west of Area I. In 1960s and subsequent years, disposal of industrial waste water into holding ponds and swales were typical on-site operations at Areas I and J. The consequences of these actions appeared in the late 1980's when analyses of ground-water quality conducted in this area revealed that these operations caused the contamination of the aquifer. In particular for Areas I and J, the quality analyses indicated the presence of VOCs in the ground-water. Figure 8 depicts the site map and the cis-DCE plume in ground-water Areas I and J in 1999 (Dames and Moore 1999).

3.3.3.2. Site Hydrogeology

NAES Lakehurst is located in the Atlantic Coastal Plain. The uppermost aquifer is the Cohansey Sand Formation which is exposed throughout most of the county surface. This formation is permeable and constitutes one of the principal aquifers in the Ocean County. In the vicinity of the NAES, this formation has reported as being a characteristically yellowish-brown, unfossiliferous, cross-stratified, pebbly, ilmenitic fine to very coarse-grained quartz sand that is locally cemented with iron oxide. Based on excavations conducted within the NAES borders, the upper 20 to 100 feet of strata underlying the center is primarily a fine to coarse grained quartz sand. Fine gravel and silt is commonly present intermixed with the sand. The depth of bedrock in the surrounding area of the NAES Site is approximately 1,800 feet. Pumping tests conducted in

the main aquifer of Area I yielded values for the horizontal hydraulic conductivity between 63 and 99 ft/day. The water table is typically shallow with regional values fluctuating between 6 and 40 feet below the surface. The regional horizontal flow rate has been reported to be 4 ft/day. However, Dames and Moore (1999) reported that the flow rate at the site is significant lower (0.15 ft/day).
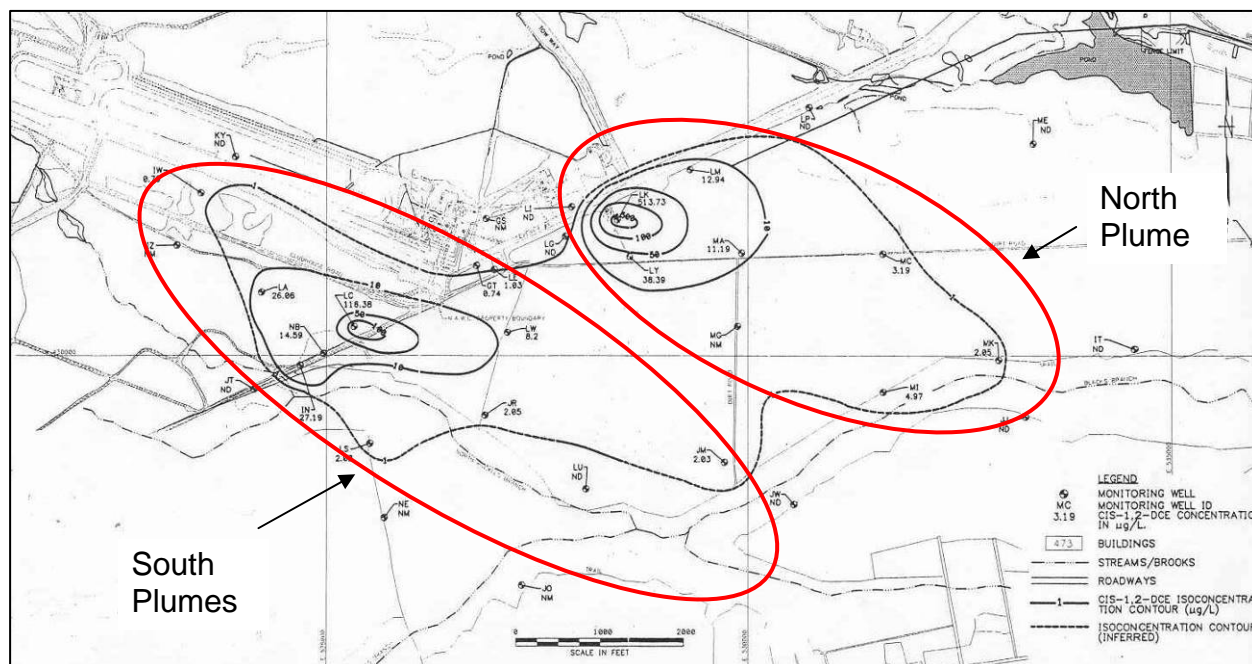
Figure 8. Site map of Areas I and J at NAES Lakehurst, NY. (Ref: Dames and Moore, 1999)

3.3.3.3.   Source and Plume Description

The contamination in Areas I & J at are primarily due to the discharge of water containing TCE, hydraulic fluid and ethylene glycol, along with the steam-cleaning operation of equipment. The monitoring program revealed the existence of three VOC plumes; one North plume and two South plumes (Figure 8).   The highest levels of contaminant are registered in deep wells (between 50 and 70 feet depth) in all three plumes. The North plume starts in a region close to Site 25, and then, contaminants are transported by the ground-water system in the east direction approximately 5.000 feet. This plume is widely spread due to changes observed in the flow direction. The South plume nearest North plume (SP1) seems to have its source in the area covered by Sites 6, 7, and 24. The contaminant released in this area has been transported 4.000 feet in the east direction. The second South plume (SP2) moves from an area close to Site 3 towards the south-east a distance of 3.000 feet. The predominant constituent in these three plumes is cis-DCE. The concentration data suggest that the plumes are in steady state and that natural attenuation (biotic) is taking place (Dames and Moore 1999).

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3.3.3.4. Redox Conditions

The redox conditions existing in the aquifer were determined by using the information collected since 1996. This data set is composed of oxygen, Fe(II), ORP, pH and other parameters. The aquifer is primarily anaerobic in nature, but with limited redox parameters, the nature of anaerobic terminal electron acceptor processes (TEAPs) can not be determined. Approximately 2,400 ft downgradient of the source zone of the north plume, the redox condition of the aquifer is aerobic. Contaminant data in the source well clearly supports that the redox conditions existing in the aquifer promote the reductive dechlorination as the preferential biodegradation process.

3.3.3.5. Past and Current Remediation Approaches

The first remedial alternative proposed to clean the aquifer was a ground-water recovery, treatment, and recharge system. Later, a study conducted in late 1993 and early 1994 revealed that this system was not going to be effective in removing the contaminant. Furthermore, it will cause the loss of several acres of wetland. Instead, an MNA-based approach was proposed as a new remedial alternative to restore the aquifer. The MNA remedial alternative started in 1996 and it has proved to be efficient in degrading the CVOC plume in Areas I and J. The data collected during this monitoring program has shown that existing geochemical and biological conditions at site are stable.

3.3.4. Hill AFB, UT – OU2

3.3.4.1. History of Operations

Hill Air Force Base (AFB) in Ogden, Utah has been a working Army and Air Force facility since 1920 and has supported a variety of manufacturing, storage, distribution, airplane maintenance, and missile storage operations.   These operations generated and used wastes including chlorinated and non-chlorinated solvents, degreasers, and fuels. In 1987 Hill AFB was placed on the EPA's National Priority List (NPL) under CERCLA and the research and remediation processes have been ongoing since then.   Operable Unit 2 (OU2) is one of the several contaminated sites existing within Hill AFB. This site, along the northeastern boundary of the base was used as a dumping site of an estimated 45- to 50-thousand gallons of chlorinated organic solvents and degreasing agents from 1967 to 1975. DNAPL sources were composed primarily of TCE with smaller amounts of tetrachloroethene (PCE) and 1,1,1- trichloroethane (1,1,1-TCA) and were dumped in unlined trenches and have contaminated the underlying aquifers. Figure 9 depicts the site map and the TCE plume in the ground-water system at OU2 in 2003.
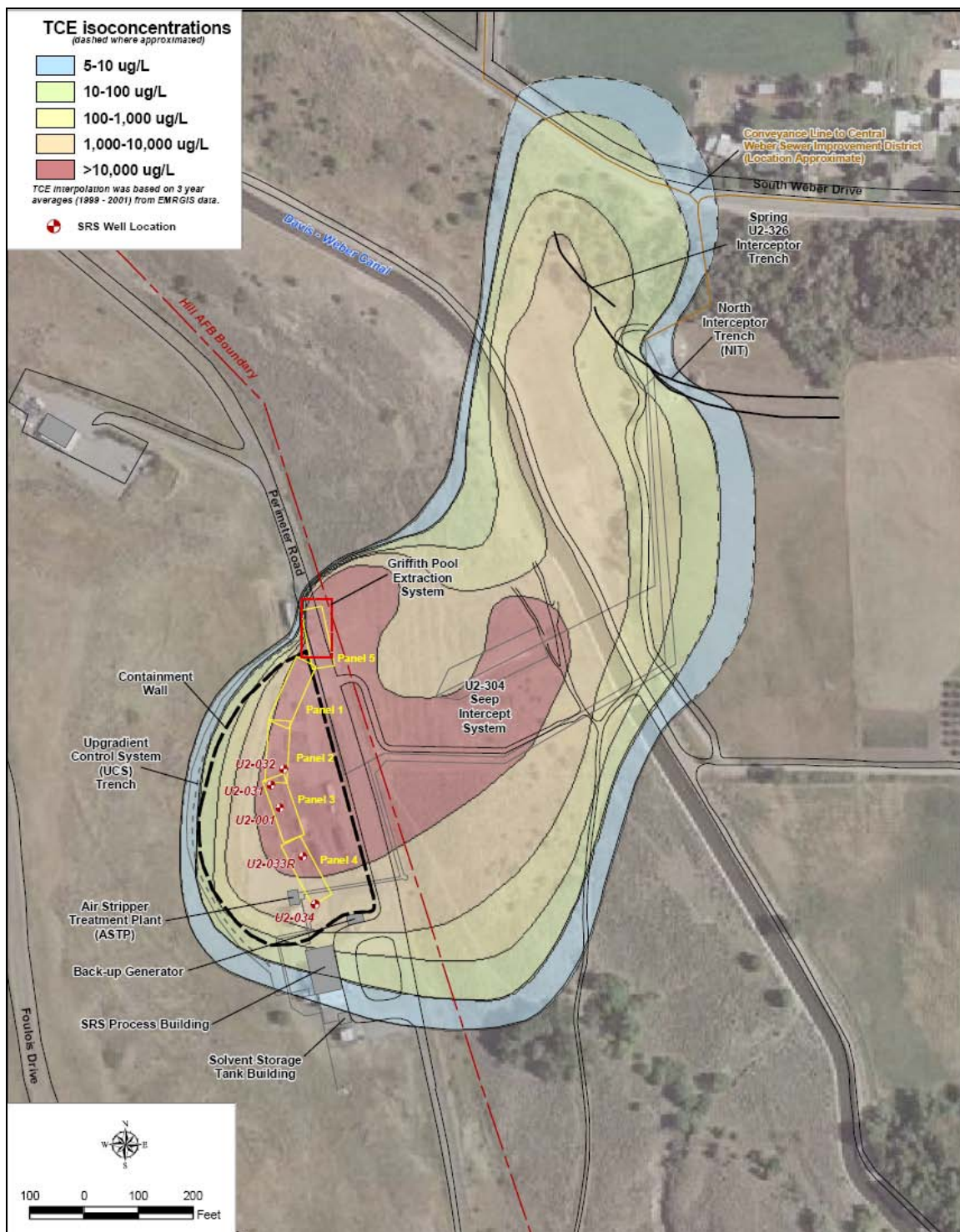
Figure 9. Site map of OU2 at Hill AFB Ogden, UT. (Ref: Air Force Center 2003)

3.3.4.2. Site Hydrogeology

Three major geological formations dominate the geology of the OU2 site. The source area is located in the shallow region of the Provo Formation. Contaminant migrated vertically through this formation so the Alpine and Weber Formations are the main regions considered for plume simulations. The Provo Formation is composed of unconsolidated silts, sands, and gravels. This formation is located at the topographic high of the contaminated site. The underlying clay aquifer has a complicated topography with a paleochannel eroded into the surface of the clay aquitard. The Alpine Formation and Weber River Floodplain are located North/Northwest of the source area and have been contaminated through transport. Understanding the location and features of the separate formations is needed for simulating ground-water flow and contaminant transport at this site.

3.3.4.3. Source and Plume Description

Over the next 30 years the high density, low viscosity, and low solubility DNAPL has formed pools in low-lying areas of the underlying clay aquitard and has migrated north/northeast in the direction of ground-water flow. Due to the geology of the site, the source contaminant has settled into approximately five separate relative topographic low points present in the clay paleochannel underlying the dumping site (Figure 10). A TCE plume derived from the source zone extends nearly 1,500 ft (Figure 9).
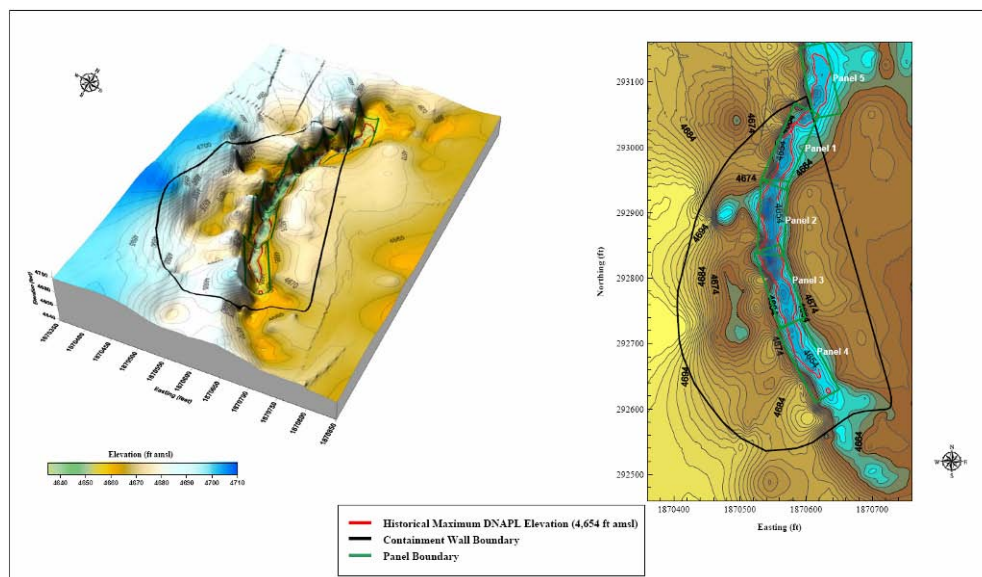
Figure 10. OU2 source area (Ref : Air Force Center 2003).

3.3.4.4. Redox Conditions

The redox conditions at OU2 were determined by using the information collected in January 2002. This data set consists of DO, nitrate, Fe(II), and sulfate. The aquifer is aerobic in nature with DO above 2.7 mg/L. The lack of Fe(II) is consistent with aerobic conditions. There is also no apparent trend in nitrate and sulfate concentrations along the ground-water flowpath. As a result, attenuation of the TCE is primarily attributed to physical processes.

3.3.4.5. Past and Current Remediation Approaches

Several remedial actions focusing on the removal of DNAPL and prevention of plume expansion have taken place since this site was added to the NPL. Most resources have been expended in source recovery and remediation in the source zone. Remediation began in 1993 with the implementation of the source recovery system, which includes a ground-water recovery well field and process treatment facility. In 1996, a slurry containment wall reaching to the underlying clay aquitard was constructed to 1) encompass most of the source area and minimize the volume of clean ground-water entering the source zone and 2) provide a barrier to the movement of contaminants form the source zone to the non-source area. After the construction of the containment wall an additional DNAPL pool was discovered outside the wall; this part of the source zone located outside of the containment wall was labeled as panel 5. In 1997, the Griffith Pool DNAPL extraction system, a system of 17 extraction wells installed in and around panel 5, was installed. From 1992 to 2002 several individual experimental DNAPL recovery operations and innovative remediation techniques were implemented in the source area and have resulted in a total DNAPL recovery of approximately 43,823 gallons, or approximately 90% of the estimated initial source volume (Air Force Center 2003).

Measures have been taken to prevent plume expansion in the non-source area as well. Interceptor trenches were constructed to collect contaminated ground-water flowing through the aquifer and pump this water to a treatment facility. The North Interceptor trench, which was constructed near the leading edge of the contaminated ground-water plume, was intended to intercept the ground-water with TCE concentrations greater than 5 µg/L before it spread contamination further downgradient. The Spring U2-326 Interceptor Trench was built two years after the construction of the North Interceptor Trench to extend the region of ground-water interception northwestwardly. The Spring U2-304 Seep Interceptor Trench was installed to collect ground-water from the center of the plume, but this trench has remained dry for most of its operational life. A total of 3 trenches have been constructed but are fairly shallow in relationship to the depth of the aquifer and their impact of ground-water flow and contaminant interception is questionable (Air Force Center 2003).

3.3.5.   NSB Kings Bay, GA – Site 11

3.3.5.1.   History of Operations

Naval Submarine Base (NSB) Kings Bay encompasses more than 16,000 acres near the Georgia-Florida border in Camden County, GA. Commissioned in 1978, the base originally served as a forward refit site for submarine squadrons. In 1980 the base was designated as U.S. Atlantic Fleet home port to the next generation of ballistic submarines. NSB Kings Bay also maintains and operates administration and personnel support facilities. Site 11 is the location of a former 25-acre landfill at NSB Kings Bay, known as the Old Camden Country landfill that was operated by the county during the mid-1970s to 1980. A variety of wastes from the local Kings Bay community and the Navy were disposed of in the landfill, including solvents and municipal waste, in unlined trenches. In the 1990's a chloroethenes plume (Figure 11) was discovered to be migrating from a PCE source zone (Chapelle et al. 2005).

3.3.5.2.   Site Hydrogeology

NSB Kings Bay is located in the Atlantic Coastal Plain. The study site is underlain by marginal marine sediments of barrier island and back-barrier lagoon origin. The most permeable sands underlying the site are present between depths of 10 and 13 m below ground surface (bgs). This permeable zone is underlain and overlain by finer-grained sands and clays of back-barrier lagoon origin characterized by lower hydraulic conductivity. Hydraulic conductivity of the permeable zone is 3 m/d based on aquifer tests and lithologic data. An organic-rich layer of soil overlying the aquifer at depth of ~3 to 5 m bgs has an important role in natural attenuation by removing DO from recharge waters. Ground-water velocity based on tracer data ranges from 10 to 20 m/yr (Chapelle et al. 2005).

3.3.5.3.   Source and Plume Description

Source zone investigations conducted in the mid to late 1990s revealed a 120-ft long by 40-ft wide PCE source with the characteristics of a DNAPL at a depth of 30 to 40 feet bgs. PCE concentration in source zone ground-water samples ranged 3.5 to 8.5 mg/L. A plume of CVOCs flowed in the ground-water toward a residential area located outside the facility to the west of the landfill. Reductive dechlorination promoted by reducing conditions in the aquifer resulted in biotransformation of PCE and TCE to cis-DCE and VC along the ground-water flowpath. Redox processes favoring anaerobic direct oxidation at the toe of the CVOC plume resulted in the oxidation of VC to carbon dioxide (Chapelle and Bradley 1998).

3.3.5.4.   Redox Conditions

The redox data (DO, Fe(II), nitrate-nitrite, sulfate, methane, and H_2) have been collected and assessed since 1997. Chapelle and Bradley (1998) describe the aquifer as anaerobic with a mix of sulfate-reducing and methanogenic conditions in the source zone. Increasing levels of Fe(II)

along the ground-water flow path and H_2 concentrations < 0.8 nM indicated iron-reducing over approximately the latter end of the plume.
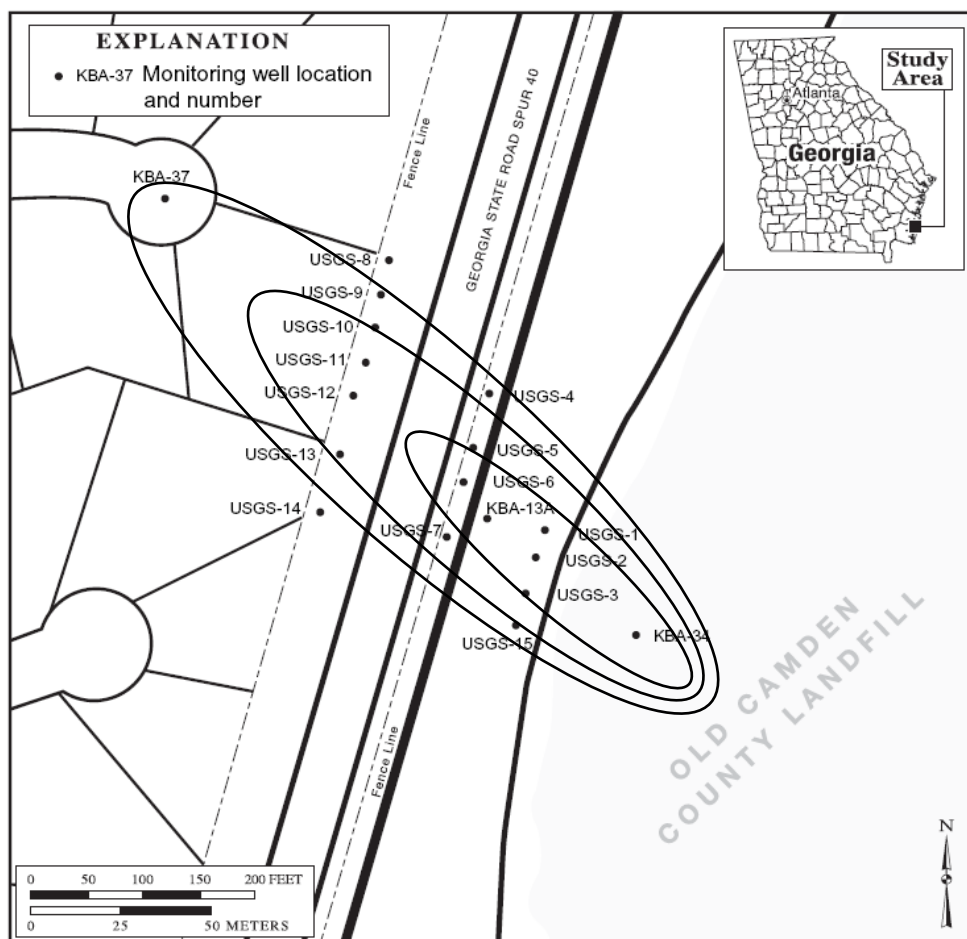
Figure 11. Chloroethene plume and monitoring wells at Site 11, NSB Kings Bay. (Ref: Chapelle, F.H., P.M. Bradley, and C.C. Casey, 2005)

3.3.5.5. Past and Current Remediation Approaches

Following a RCRA Facility Investigation (RFI) conducted in the early 1990's, pumping wells were installed to exert hydraulic control on the plume as an interim measure. Beginning in 1998, a source zone ERA was implemented, consisting of in situ chemical oxidation using Fenton's reagent followed by injection of emulsified vegetable oil. The latter component was designed to promote a return of redox conditions favorable to reductive dechlorination so that MNA could be employed as the final remediation step. The successful removal of the PCE source and subsequent plume reduction has been documented (Chapelle et al. 2003; 2005).

3.3.6. NAS Cecil Field, FL – Site 3

3.3.6.1. History of Operations

Naval Air Station Cecil Field (NASCF) is a former naval air station established in 1941 that provided facilities, services, and material support for naval operations, officially closed in 1999. The facility is located in southwestern Duval County, Florida within the Jacksonville city limits. The main facility occupies 9, 516 acres. Some of the operations at the facility included operation of fuel storage facilities as well as intermediate level aircraft maintenance. In 1989 the installation was placed on the NPL due to waste sites located at the facility. NASCF is a closed naval air station that was part of the 1993 and 1995 Base Realignment and Closures (BRAC).

Site 3 is a vacant area located at the end of an active aircraft runway on the perimeter of NASCF. It was a disposal pit that was used to dispose of liquid wastes (oil) and sludge. The period disposal operations began at the site is uncertain. A review of aerial photographs during the RI suggested the area was not disturbed prior to 1960, and records detailing this disposal activity are absent. However, base disposal operations were expected to have begun during the late 1950's/early 1960's and ceased by 1975. Wastes products potentially disposed at the site include fuels, oils and solvents. Wastes were reportedly drained into the pit from portable bowsers or 55-gallon drums and allowed to evaporate and/or seep into the ground. The liquid wastes were periodically burned by the NASCF fire department when the wastes reached the top of the shallow pit (ABB-ES 1996). Investigation of shallow ground-water contaminated from these operations was determined to exceed risk-based criteria and require remediation.

3.3.6.2. Site Hydrogeology

The topography of the site is relatively flat. From the disposal pit, the site gently slopes towards Rowell Creek (Figure 12). The impacted water bearing system in this area is the surficial aquifer. Previous descriptions (ABB-ES 1996) characterize it is an unconfined system that is encountered at a depth of 3 to 5 feet bgs near the location of the disposal pit and extends to a depth of approximately 50 feet bgs. The average horizontal hydraulic gradient is approximately 0.005 foot per foot (ft/ft) at the waste disposal pit and increases to 0.035 (ft/ft) close to the creek. Ground-water flows in an eastern direction and discharges into Rowell Creek.

The site lithology for the upper surficial aquifer from land surface to approximately 50 feet bls has been described (ABB-ES 1996) as consisting of fine to medium-grained, poorly sorted quartz sand with some interbedded sandy clay, clayey sand and silty clay sand layers. A less permeable layer of sandy clay, clayey sand and clay of approximately 20 feet is located directly beneath this unit. An aquifer test (Halford 1996) conducted in the upper zone of the surficial aquifer near Site 3 provided estimates of hydraulic conductivity in the range of 3-5 ft/d. Assuming an effective porosity of 0.3, the seepage velocity is estimated to range from 18-30 feet/year near the source area. This is expected to increase as the gradient becomes steeper near Rowell Creek.
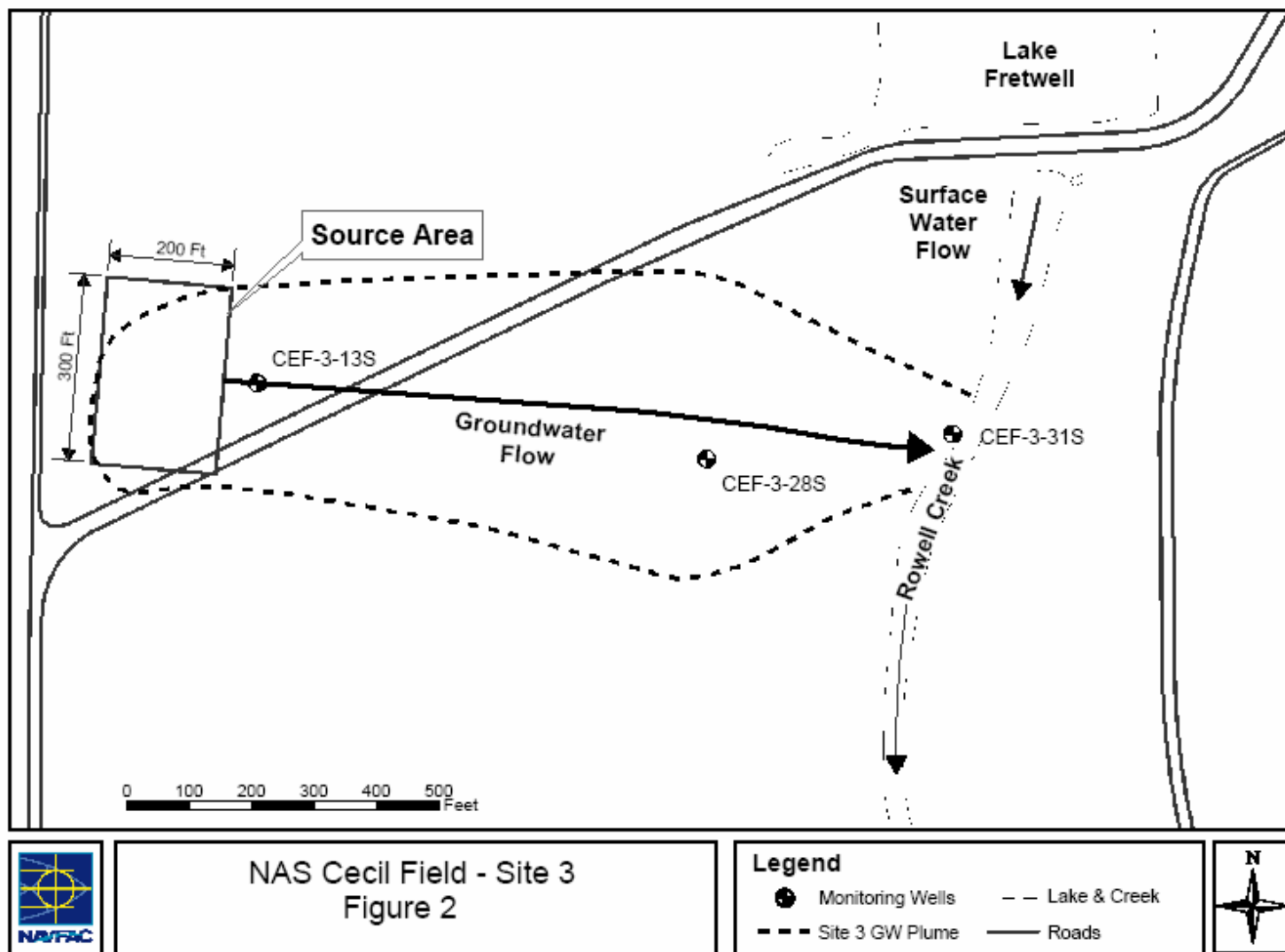
Figure 12. Site map of Site 3 at NAS Cecil Field, FL. (Ref: NAVFAC report, 2006).

3.3.6.3.   Source and Plume Description

Chemicals of concern in ground-water identified during the RI included VOCs, semi-volatile organic compounds (SVOC's) and a polychlorinated biphenyl (PCB). The precise dimensions of the disposal pit are uncertain.   The lateral extent of the historical pit has been described differently in historical reports. One report (ABB 1997) identifies the pit as having a diameter of from 50 to 100 feet, while another report indicates it consisted of a larger trench. Although the actual amount and composition of the waste disposed is not well known, the results from the RI identified the presence of VOC's and SVOC's consistent with waste oils and degreasing solvents. Soil and water samples collected during the RI were used estimate the source area to be approximately 300 feet by 200 feet. Low levels of VOC's extend to a depth of at least 40 feet below land surface; however, the bulk of contamination appears to be in the upper 20 feet of the saturated zone. TCE concentration in the source zone was 1,490 μg/l prior to source ERA. The VOC plume is approximately 1,300 ft long and discharges into Rowell Creek (Figure 12).

3.3.6.4.   Redox Conditions

Geochemical parameters related to microbial metabolic processes have been collected at the site since 1997 to ascertain the efficiency of intrinsic biodegradation. Parameters collected included: DO, nitrate, ferrous iron, manganese, sulfate, sulfide, methane and pH. Interpretation of the site geochemistry suggests the shallow aquifer is iron-reducing from the source area down past the middle of the plume where it eventually becomes mildly oxic to iron reducing at different times prior to movement through the bed sediments in the creek. For the chlorinated ethenes, iron-reducing conditions are sufficient for microbial reduction of TCE to DCE if a sufficient supply of electron donors is available. In the aerobic streambed sediments at the discharge zone, site specific monitoring and laboratory studies have shown that VC and DCE can be oxidized to CO_2 (Bradley and Chapelle 1996). For the SVOC's such as the dichlorobenzenes and naphthalene, the rate of degradation is expected to be lower under anaerobic conditions near the source area, but due to their slow rate of transport this may be compensated with additional time for anaerobic degradation along the flowpath. Aerobic conditions at the distal portion of the plume are expected to increase the rate of degradation as they eventually move into this region.

3.3.6.5.   Past and Current Remediation Approaches

A ROD for ground-water contamination at Site 3 was signed in 1998. The regulatory framework used to develop the ROD included the CERCLA, the National Contingency Plan (NCP) and the Florida Department of Environmental Protection (FDEP), Florida Administrative Code 62-550 and public comments. The remedy selected to address contaminants in ground-water included a combination of alternatives: In situ air stripping of source area ground-water by air sparging, MNA of downgradient ground-water and implementation of institutional controls using deed restrictions to limit the use of contaminated ground-water.   Air sparging was conducted intermittently from 1999 to 2002. The site is currently in the monitoring phase of MNA.

3.3.7. NAS Pensacola, FL – WWTP

3.3.7.1. History of Operations

NAS Pensacola occupies approximately 5,800 acres on a peninsula in southern Escambia County, 5 miles south of Pensacola, FL. The on-site waste-water treatment plant (WWTP) has been used to process wastewater since 1941, when the sewage treatment facility was first installed. During the 1950's and 60's, the WWTP received industrial waste from paint and electroplating operations. Much of this waste was processed concurrently with sewage waste. In 1971, the WWTP was upgraded to separate the treatment of industrial and domestic wastes. Wastewater treated at this site contained organic solvents (including chlorinated ethenes, benzene, and chlorobenzenes), phenols, chromium electroplating wastes (including cyanide and other heavy metals), and wastes from a chemical conversion coating process for aluminum. Drying beds were used to dewater the sludges generated by the waste-treatment processes. These abandoned drying beds were the source of environmental contamination that was addressed under RCRA.

3.3.7.2. Site Hydrogeology

The WWTP is underlain by marine and fluvial terrace sediments deposits of Quaternary age. Sediments exposed at land surface and extending to a depth of about 40 feet are predominantly fine to medium sands that form a shallow water-table aquifer. This water-table aquifer is underlain by lower-permeability silts and clays of marine origin that act as a confining bed. This confining bed is underlain by permeable sands and gravel that form a confined aquifer system. This confined aquifer is known locally as the "main producing zone" and has been used for water supply. At the WWTP, the confined main producing zone has higher water levels than the overlying water-table aquifer. Thus, the site is characterized by an upward hydraulic gradient. The combination of the confining bed and the upward hydrologic gradient prevents downward movement of ground-water at this site (Ensafe/Allen and Hoshall 1995). Because of this, most of the contaminants are present in the water-table aquifer between a depth of 20 to 40 feet below land surface. Pensacola Bay, located immediately adjacent to the WWTP, serves as the regional discharge area for both the shallow water-table aquifer and the underlying main producing zone.

3.3.7.3. Source and Plume Description

The chlorinated ethene plume present at the WWTP is delineated by section A-A', and the chlorinated benzene plume is delineated by section B-B' (top, Figure 13). The "hotspot" of benzene and chlorinated benzene is located near SMW-8, and is delineated by section C-C' (bottom, Figure 13). Studies by the U.S. Geological Survey beginning in 1996 (USGS 1999) indicated that conditions were favorable for natural attenuation processes to treat chlorinated ethene-contaminated ground-water. Specifically, it was shown that chlorinated ethenes were rapidly transformed to non-toxic byproducts (carbon dioxide, chloride, and ethane) prior to discharging into Pensacola Bay. Chlorinated benzenes were more recalcitrant under the ambient anoxic conditions of ground-water, but were removed at the freshwater/saltwater mixing zone of

the aquifer prior to reaching Pensacola Bay. The observed chlorobenzene removal appears to reflect the combined effects of mixing at the freshwater/saltwater interface near Pensacola Bay and biodegradation processes.

Figure 13. Site map of the WWTP at NAS Pensacola showing transects A-A' and B-B' (top) and transect C-C' (bottom). (Ref: U.S. Geological Survey, 1999)

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3.3.7.4. Redox Conditions

Geochemical parameters used to characterize redox conditions at the site included DO, Fe(II), sulfate-sulfide, methane H_2. These data show that for flowpaths A-A' and B-B', conditions are largely anoxic as they have been since redox monitoring began in 1996 (USGS 1999). These data also show that aerobic conditions appear periodically at flowpath C-C', caused by rainwater infiltrating into the aquifer at the edge of the capped drying beds (Figure 13). Because the capped drying beds are impermeable, rainfall runs off and collects at the edge of the beds where it percolates into the underlying aquifer. During the drought years of 2002 and 2003, recharge to the aquifer from this process was less in evidence. Wetter conditions in 2004, however, have dramatically increased the delivery of oxygen-containing recharge to the system. Because chlorobenzenes rapidly biodegrade under aerobic conditions, this process has serves to enhance the efficiency of natural attenuation along flowpath C-C'.

3.3.7.5. Past and Current Remediation Approaches

As part of the RCRA response, large volumes of contaminated sediments and soils were removed from the abandoned sludge drying beds (EnSafe/Allen & Hoshall 1997). The sludge drying beds and associated material were removed to a depth of six feet below land surface and disposed of as hazardous waste. The site was backfilled with clean sand, and capped with high-density asphalt. As part of these closures, a ground-water-recovery system was put in place to pump and treat contaminated ground-water.

The size of the chlorobenzene plume impacting SMW-8 was determined by geoprobing a series of holes surrounding SMW-8, sampling the ground-water at three-foot vertical increments, and analyzing the water using a field gas chromatograph (USGS 2000). Based on the results of this study, Oxygen Release Compound (ORC®) was injected along two lines on March 24, 2001, to enhance biodegradation of chlorobenzene. The line nearest the capped drying beds consisted of 12 holes spaced between four and one feet apart. The downgradient line consisted of six holes spaced four feet apart. The locations of the ORC® injection holes and the monitoring wells installed to monitor the effectiveness of this remediation are shown in Figure 13 (bottom). The ORC® was distributed as uniformly as possible between depths of 40 and 4 feet bgs as the drilling rods were removed from each hole.

After the ORC® injection, concentrations of both benzene and chlorobenzene were lowered substantially in wells ORC-1 and ORC-2. In well ORC-1, which was nearest to the first line of ORC® injection, oxygen concentrations increased soon after injection, and concentrations of benzene and chlorobenzene decreased dramatically. Concentrations of oxygen, benzene, and chlorobenzene at well SMW-8, which is eighteen feet downgradient of the ORC® injection line, show a delayed effect caused by the transport time of ground-water flowing through the ORC® line. For the first two months there was no measurable effect on concentrations of DO. By September, 2001, concentrations of oxygen increased, and concentrations of benzene and chlorobenzene decreased. Contaminant concentrations remained low until the oxygen-releasing capacity of the ORC® was exhausted, and then contaminant concentrations again increased.

However, for the time period between September, 2001 and 2002, the ORC® acted as a contaminant source-area removal operation. Ground-water chemistry data collected during this time period was selected to test the NAS software for a source area-removal action.

In 2003, rising concentrations of benzene and chlorobenzene observed in well SMW-8 resulted in an investigation of the source of the contaminants. The sediments underlying the capped drying beds were sampled with direct-push technology in a grid pattern designed to locate any "hotspots", ground-water samples collected, and immediately analyzed by gas chromatography. The results of this investigation delineated a discrete hotspot of chlorobenzene contaminants adjacent to wells ORC-1, ORC-2, and SMW-8.

3.3.8.   Alaska DOT&PF – USGS (Peger Road) Site

3.3.8.1.   History of Operations

The Peger Road facility is located in Fairbanks, AK and is operated by the Alaska Department of Transportation and Public Facilities (ADOT&PF). It and has been used as an equipment maintenance and testing facility. A variety of solvents and petroleum hydrocarbons were used on site during the 1970s and 1980s. Release of these compounds has resulted in the formation of discrete TCE, PCE, and benzene plumes that have been characterized by the Alaska Department of Environmental Conservation (ADEC). The facility continues to be operated by the ADOT&PF, and the environmental contaminants are being monitored and managed by the ADEC.

3.3.8.2.   Site Hydrogeology

The Peger Road site is underlain by alluvial sediments deposited on the floodplain of the Chena River in the Fairbanks area. These sediments are characterized by relatively high hydraulic conductivities (200-600 ft/d) with a mean value of about 400 ft/d (USGS 2004).

3.3.8.3.   Source and Plume Description

TCE, PCE, and petroleum hydrocarbons were released prior to 1998 in several different locations (Fig. 14). A plume of TCE contamination extends from the maintenance lab approximately to 19th Ave (Fig. 15). The soil zone overlying the TCE plume is characterized by permafrost, a feature which may affect vertical recharge to the aquifer. In addition, permafrost may locally affect directions of ground-water flow and thus the shape of the TCE plume (ADEC 2005). The aquifer is hydraulically connected to the nearby Chena and Tanana Rivers, and seasonal water-level fluctuations in these rivers affect hydraulic gradients in the aquifer. Rates of ground-water flow, therefore, also vary seasonally.

Figure 14. Aerial photo of the USGS (Peger Road) study site in Fairbanks, AK. (Ref: U.S. Geological Survey, 2005)

3.3.8.4. Redox Conditions

The redox conditions at the study site were determined by using the information collected in September 2003. This data set consists of DO, Fe(II), and sulfate. The ground-water in the source area wells is aerobic with DO above 2 mg/L. Elevated Fe(II) and depleted DO concentrations in wells downgradient of the source is consistent with anaerobic conditions.

3.3.8.5. Past and Current Remediation Approaches

Approximately 700 cubic yards of TCE-contaminated soil were excavated for the expansion of the Materials Laboratory on site. Excavated soil was land-spread to volatilize TCE.

3.4. Pre-Demonstration Testing and Analysis

Not applicable to the demonstration.
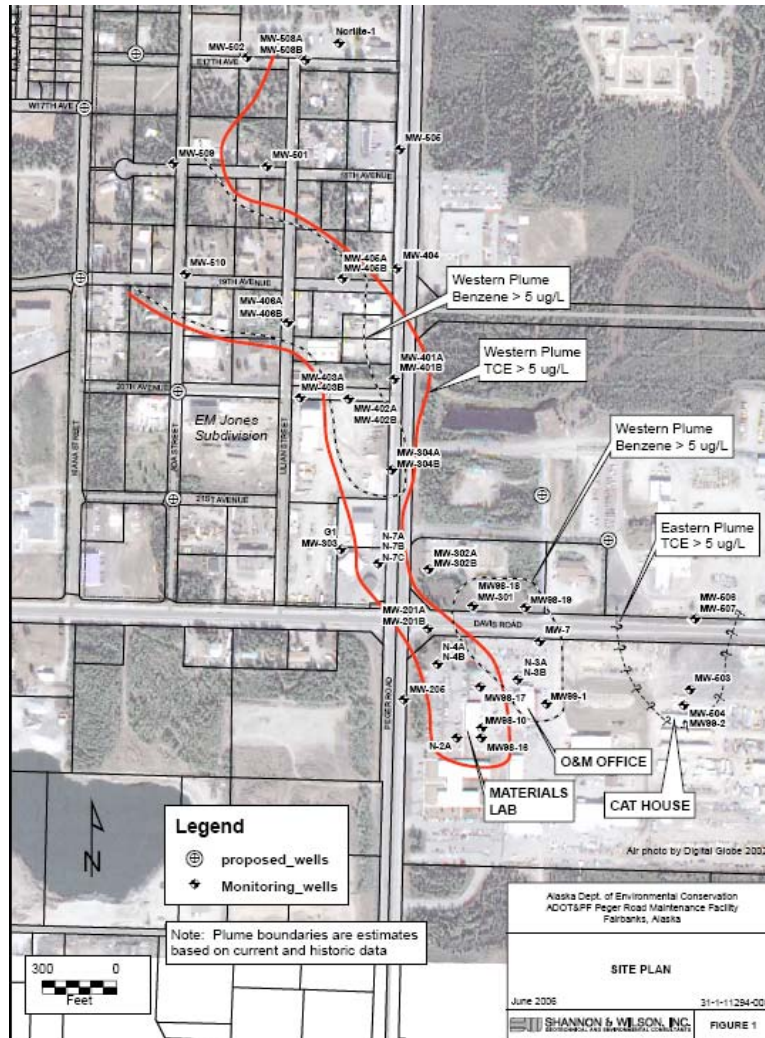
Figure 15. Well location map for the USGS study site in Fairbanks, AK (Ref: ADEC 2005).

3.5.   Testing and Evaluation Plan

All required subsections to Section 3.5 are not applicable to the demonstration.

3.6.   Selection of Analytical/Testing Methods

Not applicable to the demonstration.

3.7.   Selection of Analytical/Testing Laboratory

Not applicable to the demonstration.

4. Performance Assessment

4.1. Performance Criteria

The performance of NAS was evaluated on the basis of accuracy, versatility, reliability, and applicability as described in Table 4.

Table 4. Performance Criteria

Performance Criteria	Description	Primary or Secondary
Accuracy	NAS provides estimates of contaminant concentration changes over time. Predicted/measured contaminant concentration changes based on site monitoring data will be used to assess accuracy. As described previously, four metrics (1) predicted/measured inflection points of concentration changes, (2) predicted/measured time of breakthrough, (3) slopes of predicted/measured time-concentration profiles, and (4) predicted/measured concentration profiles of NAPL components are used.	Primary
Versatility	Site selection will identify sites from each major region of the United States, so that hydrologic conditions will vary accordingly. The versatility of NAS to different hydrologic conditions is assessed by the accuracy achievable in each hydrologic setting.	Primary
Reliability	NAS uses complex analytical and numerical simulations to obtain TOR estimates. Implementation of NAS requires that these simulations run reliably. Reliability can be quantified by comparing the number of simulations performed to problems encountered.	Secondary
Applicability	NAS is a screening tool and is not designed to apply to all sites. Nevertheless, NAS should be flexible enough to be applied to more than half of the sites considered. During site selection, a record will be kept of sites considered, and sites to which NAS is deemed applicable. As stated in Section 3.2, the selection criteria will include: • Five years of annual monitoring data that includes both the geochemical and contaminant chemistry and water levels. • Ground-water velocities exceeding 5 ft/year • Darcy flow (i.e., not conduit flow) • Unidirectional ground-water flow fields and boundary conditions that can be reasonably simulated by the analytical code	Secondary

4.2. Performance Confirmation Methods

The effectiveness of the demonstrations was primarily evaluated based on the two primary performance criteria (accuracy and versatility). The success of each demonstration was based on the ability of NAS to attain the performance metrics and the robustness of performance over the range of sites (Table 5).

Table 5. Performance and Performance Confirmation Methods

Performance Criteria	Expected Performance Metric (pre demo) (*Examples*)	Performance Confirmation Method (*Examples*)
PRIMARY CRITERIA (Performance Objectives) (Quantitative)		
Inflection point of concentration-time curve	*The predicted inflection point (point A1, Fig. 3-1) of the concentration-time curve should coincide with the observed inflection point within one year.*	*Contaminant concentration/time curves at least one mid-plume well, and preferably several, over time.*
Time of breakthrough	*The predicted time of breakthrough (point B, Fig. 3-1) of the concentration-time curve should coincide with the observed breakthrough within two years.*	*Contaminant concentration/time curves at least one mid-plume well, and preferably several, over time.*
PRIMARY CRITERIA (Performance Objectives) (Qualitative)		
Slope of concentration-time curve following inflection point	*The predicted slope of the inflection point of the concentration-time curve (slope C, Fig. 3-1) should be similar to the observed slope.*	*Contaminant concentration/time curves at least one mid-plume well, and preferably several, over time.*
Predicted/observed contaminant-concentration profiles for different components of NAPL	*More soluble components of NAPL should be removed sooner than less soluble components relative to overall NAPL composition.*	*Contaminant concentration/time curves at least one mid-plume well, and preferably several, over time.*

Each site application of NAS followed the procedure listed below with some minor variation:

1. Run NAS simulations for a range of source mass scenarios and a range of NAPL composition values;

2. Compare results to available data from source zone and down-gradient monitoring wells;

3. Determine inflection points, time of breakthrough, slope of concentration-time curve following inflection point, predicted contaminant concentration profiles, etc., and compile data for each site;

4. Compare predictions to observations (following stated quantitative and qualitative performance metrics as specified in Table 5);

5. Quantify error and perform goodness-of-fit analysis

6. Refine estimates of source zone mass and composition and return to Step 1.

4.3.   Data Analysis, Interpretation and Evaluation

Table 6 lists the TOR component of NAS that was tested for each site application. In some cases both the TOS (analytical solution) and the TND (numerical solution) were tested. Also included in the table is the technology employed at the source zone. At some sites, no ERA was employed but monitoring well data trends showed depletion of contaminant mass and concentration under natural ground-water flow or under an induced gradient from pumping. Results are presented for each site, and then an overall assessment of each component (TOS and TND) is provided at the end of this section.

Table 6. Summary of TOR Component Tested for each Site Application

Site Application	TOR Component Tested	Source Zone ERA
Seneca Army Depot – Ash Landfill	TOS	Excavation
Niagara Falls – USGS Study Site	TND	Pump-and-Treat with depletion
NAES Lakehurst – Sites I & J	TND	Natural depletion
Hill AFB – OU2	TOS	Containment (barrier wall)
NSB Kings Bay – Site 11	TOS	Chemical oxidation (Fenten's)
NAS Cecil Field – Site 3	TND	Air sparging
NAS Pensacola – WWTP	TOS	ORC
Alaska DOT – USGS Study Site	TOS	Excavation
ERA = engineered remedial action ORC = oxygen release compound TND = time of NAPL dissolution TOS = time of stabilization		

4.3.1. Seneca Army Depot, NY – Ash Landfill

Between August 1994 and June 1995 a partial source removal was conducted at the Ash Landfill located in the Seneca site. The remedial action consisted of excavation and thermal treatment of VOCs impacted soils. After the soil was treated, it was backfilled into the excavation area. Source zone monitoring well data show that complete remediation was not achieved and that hot spots of contamination remained. Specifically, TCE concentration in the source zone declined from 12,000 to 5,300 µg/L. As a consequence of this partial source removal, the concentration levels at the downgradient wells showed a declining trend with time but not to levels expected if the source were completely removed. For predicting the impact of complete excavation on DOS and TOS, the source zone concentration input to NAS would be zero. In this case, the observed post-remediation source zone TCE concentration was used as input to NAS.

Figure 16 shows the stable pre-remediation TCE plume and the best-fit analytical solution using data collected immediately prior to the completion of the source excavation. Due to the lack of DCE concentration data before the partial source treatment period, the NAS application was based entirely on the TCE data. For the purpose of implementing the DOS/TOS feature, the field-observed TCE source concentration following source excavation was used as input to NAS. NAS was then used to simulate concentration versus time at wells PT12A and PT22, located at distances of 180 and 400 ft downgradient of the source, respectively.
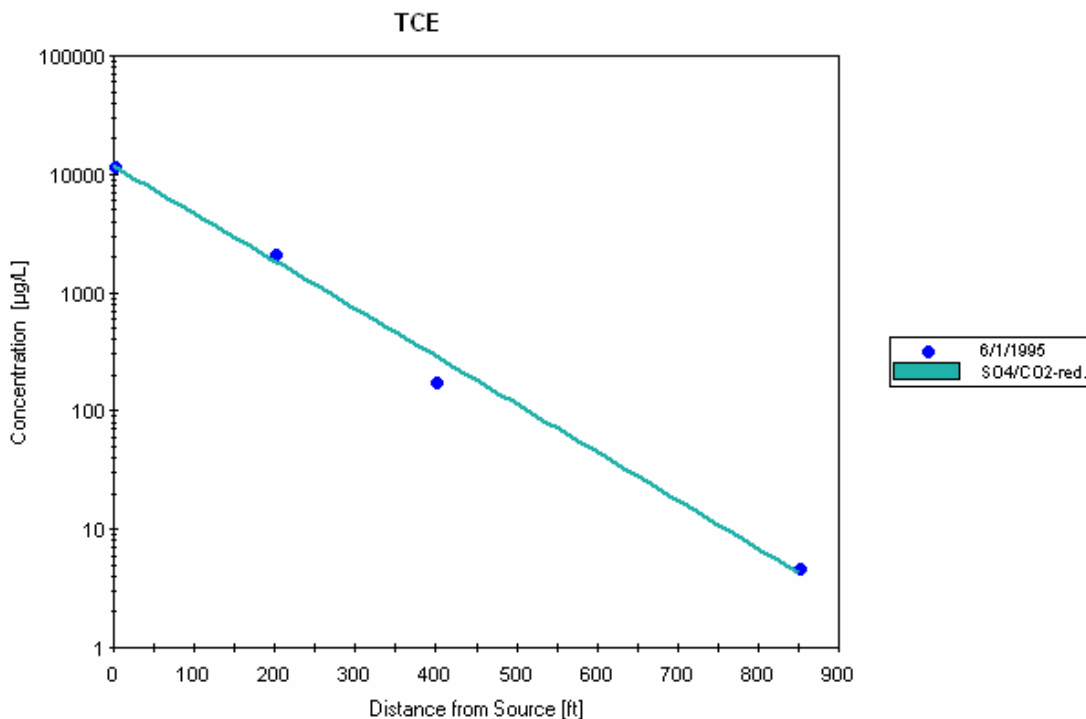
Figure 16. Observed and NAS-simulated TCE concentration versus distance along plume centerline prior to source concentration reduction.

Breakthrough curves at wells PT12A and PT22 are shown in Figure 17. Data gaps in the mid-1990s and along with the time fluctuation in concentrations, hinders the accurate estimation of the observed breakthrough time and concentration slopes. The inflection points are difficult to judge from the data, but in general, a reasonable fit was obtained at both wells. Analysis of the hydraulic gradient indicated seasonal variability in the flow direction in the vicinity of the source. Variability in the ground-water flow combined with the reduction in the source width following excavation provides a reasonable explanation for the fluctuation in VOC concentrations over time. Use of the field-observed TCE source concentration resulted in an excellent fit to the final observed concentration at PT21A, but a poorer fit to the data is noted at PT12A. The inability of NAS to match the final concentration at PT21A is due to the reduced source volume and the repositioning of the plume centerline following source excavation.
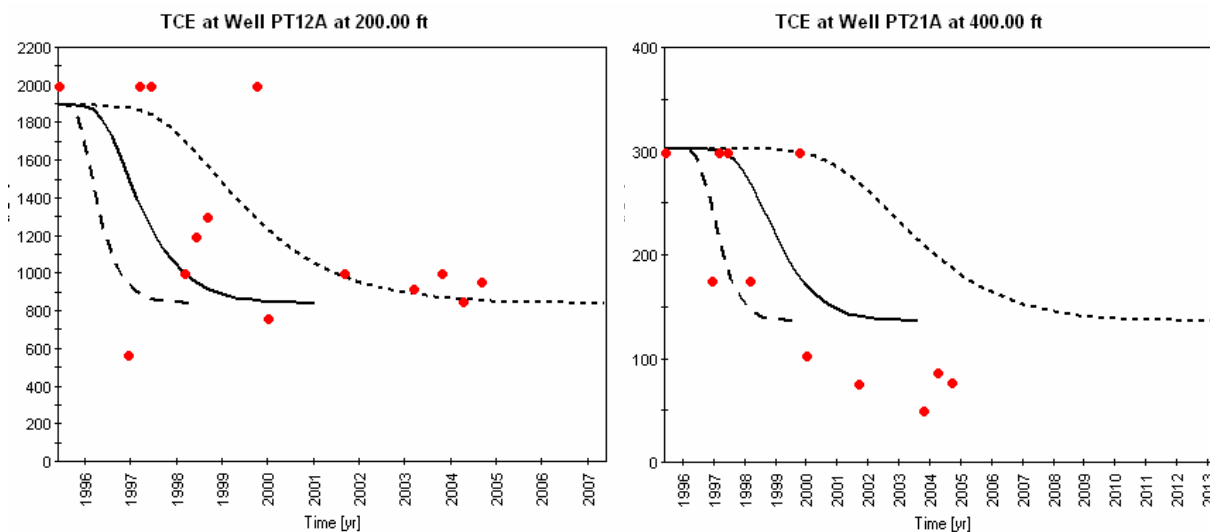
Figure 17. Observed and NAS-simulated TCE concentration versus time at downgradient wells based on the observed source concentration reduction.

4.3.2.   Niagara Falls, NY – USGS Site

For the purpose of this application, NAS was modified to allow the user some flexibility in specifying which well will be the observation point at which the TOR concentration versus time estimates are evaluated (originally always set to the first concentration well). This change was implemented to enable simulation of a downgradient monitoring well where concentration trends showed steady declines following the initiation of the system of pumping wells in 1993. Thus, the position of the observation well for the TND option is moved to a user-defined well located further downgradient of the source.

The approach taken for the NAS application was to vary input parameters (NAPL Mass and average saturated thickness) to find the best correlation between NAS-estimated TCE concentration-versus-time curves and observed data. NAPL Mass ranged from 1,000 to 100,000

kg and the average saturated thickness ranged from 3.5 to 10 ft (approximated from Yager 2002). Figures 18 and 19 provide a comparison of the sensitivity of the average saturated thickness on the NAS-simulated TCE concentration versus time at Well 87-20(1). NAS simulations using the pump-and-treat option provided a more favorable match with the observed data compared to the MNA option with no pumping well.
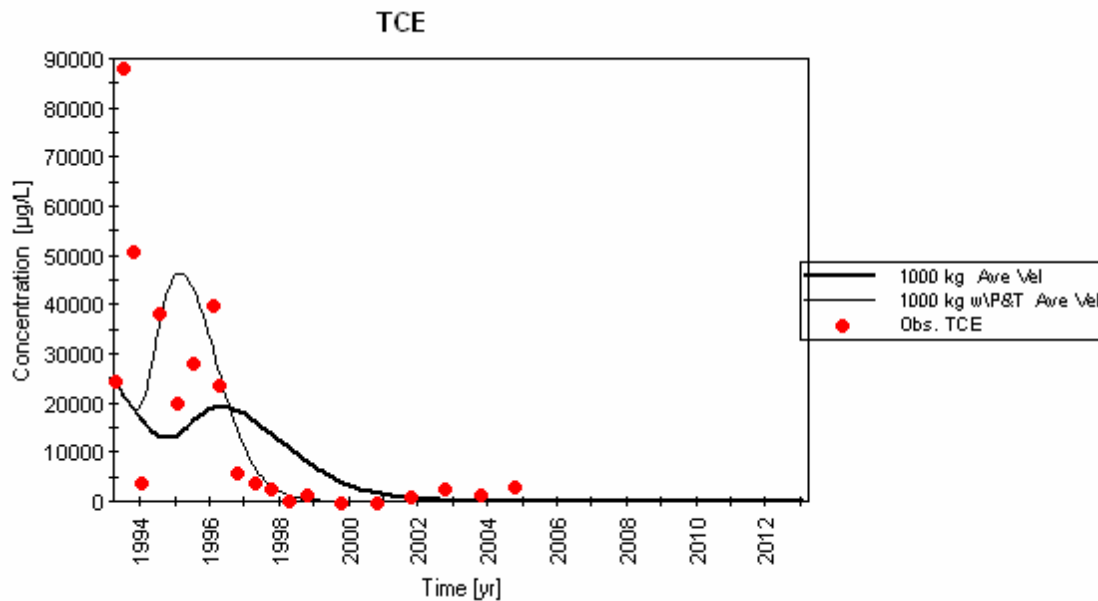
Figure 18: NAS-calculated vs. observed TCE – Average saturated thickness =6.75 ft.
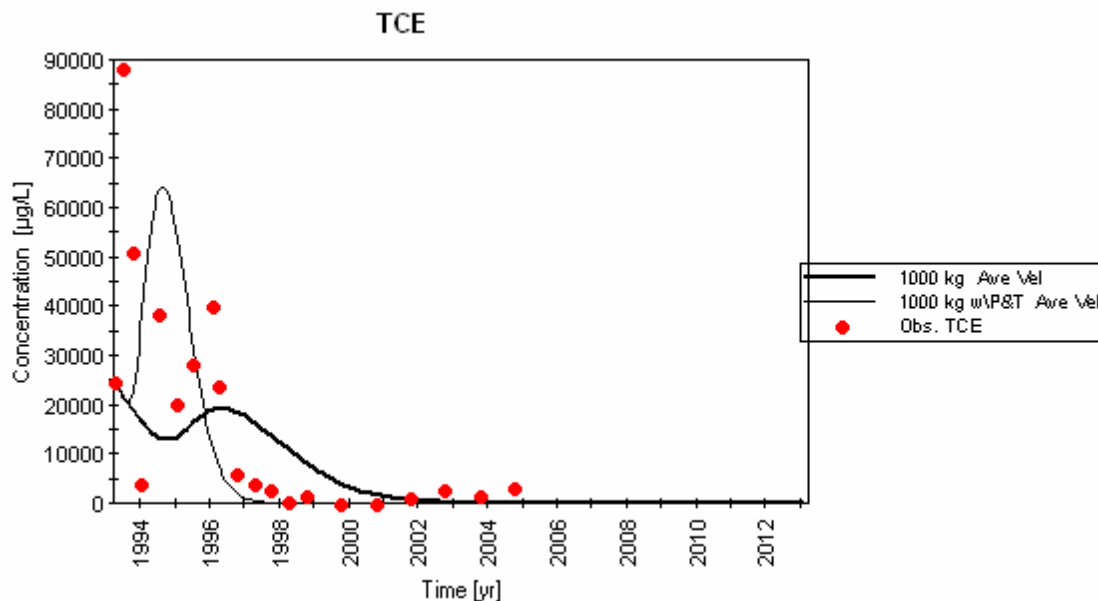
Figure 19. NAS-calculated vs. observed TCE - Average saturated thickness =3.50 ft.

4.3.3.   NAES Lakehurst, NJ – Sites I&J

The NAS tool was employed to predict the decline in aqueous concentration resulting from the dissolution of the NAPL source at a nearby downgradient monitoring well.   Source characterization efforts in the field were not extensive and a representative source zone monitoring well (LK) was selected for the application. Because the composition and location of the source could not be well-defined during the monitoring program, two hypothetical source compositions were modeled using NAS: 1) single-composite NAPL source (total chlorinated ethenes), 2) multi-constituent NAPL. The objective was to investigate the two different approaches in dealing with the uncertainties in source parameters.   Because the source was neither removed nor treated, the comparison between the predicted curve and the existing data is only feasible using a qualitative approach.

For both cases, the predicted curves reasonably match the field data. In regards to the source compositions, the single compound assumption yields to a source mass ranging from 8,000 kg to 9,000 kg and a mass fraction of 0.05 (Figure 20). TND estimates using NAS are also compared with other methods: A simple extrapolation method using regression (all data) and results of a comprehensive numerical model using the code RT3D. Unlike SEAM3D which employs a mass balance approach to the source term, depleting sources in RT3D were manipulated by the model users through the implementation of a time-varying boundary condition.
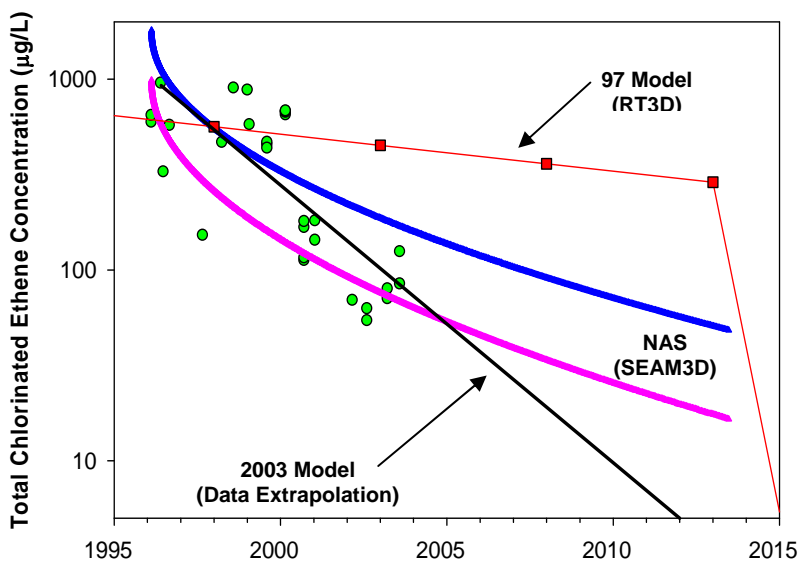
Figure 20. Observed concentrations of total chlorinated ethenes for single-component source models using NAS and RT3D. A data regression is also shown.

In comparison, by including three CVOCs in the NAPL (PCE, TCE, and DCE) a greater source mass (23,000 kg) was required. The total mass fraction of CVOCs is 0.101. This result suggests that the contaminant source in this site is rather diluted, which is consistent with information

gathered from the on-site operation reports that describe the dumped substance as a combination of water-soluble hydraulic fluid, ethylene glycol, trichloroethene, and lubricating oil. Figure 21 reflects a pattern that is usually observed with sources with multiple compounds and shows that the dissolution curves of TCE and DCE can be reasonable reproduced by NAS. The dissolution curves for total chlorinated ethenes in Figure 21 did not match the observed data relative to the curve shown in the single-CVOC NAPL simulation (Figure 20).
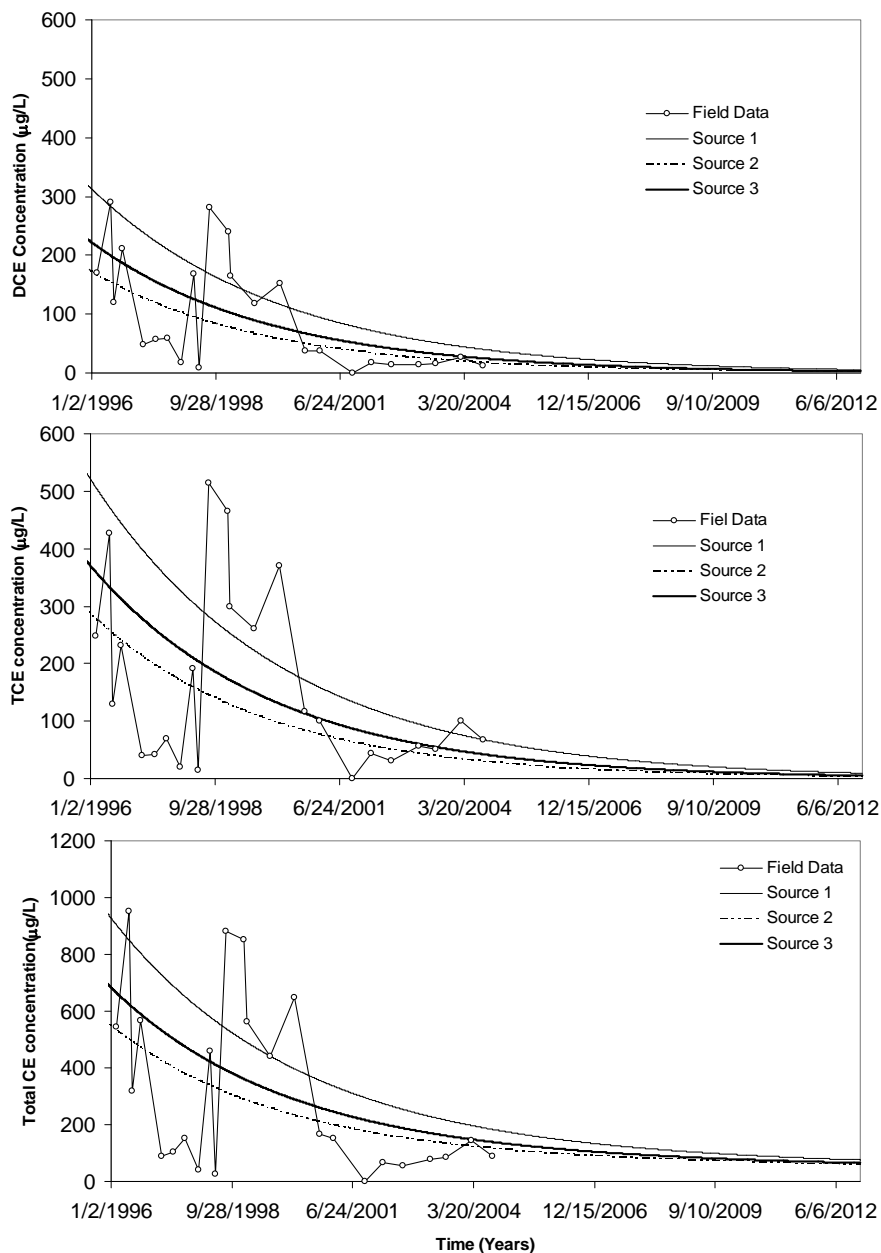
Figure 21. NAS-simulated versus observed concentrations of TCE (top), DCE (middle), and total chlorinated ethenes (bottom) for the multi-component source model.

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4.3.4.   Hill AFB, UT – OU2

Analytical solutions used in NAS are based on the assumption that the hydrostratigraphic unit is homogeneous so that contaminant velocities do not vary along the entire length of the plume. At OU2, NAS was applied to data from monitoring wells located in the Alpine formation (closest to the wall) and 16 ft downgradient of the interface between the Alpine and Weber formations. The TCE simulations shown in Figure 22 are based on hydraulic conductivity representative of the Alpine formation but with two different values of the horizontal hydraulic gradient. A recharge mound near the containment wall resulted in a steep hydraulic gradient and high velocity (1.8 ft/d). An improved fit to the data at both wells was observed using a velocity (0.6 ft/d) representative of conditions downgradient of the wall. The range in TOS results reflects variability in the fraction of organic carbon. Although NAS was not specifically designed to simulate the effects of a containment wall on a plume, these results suggest that NAS is versatile and useful in this application.
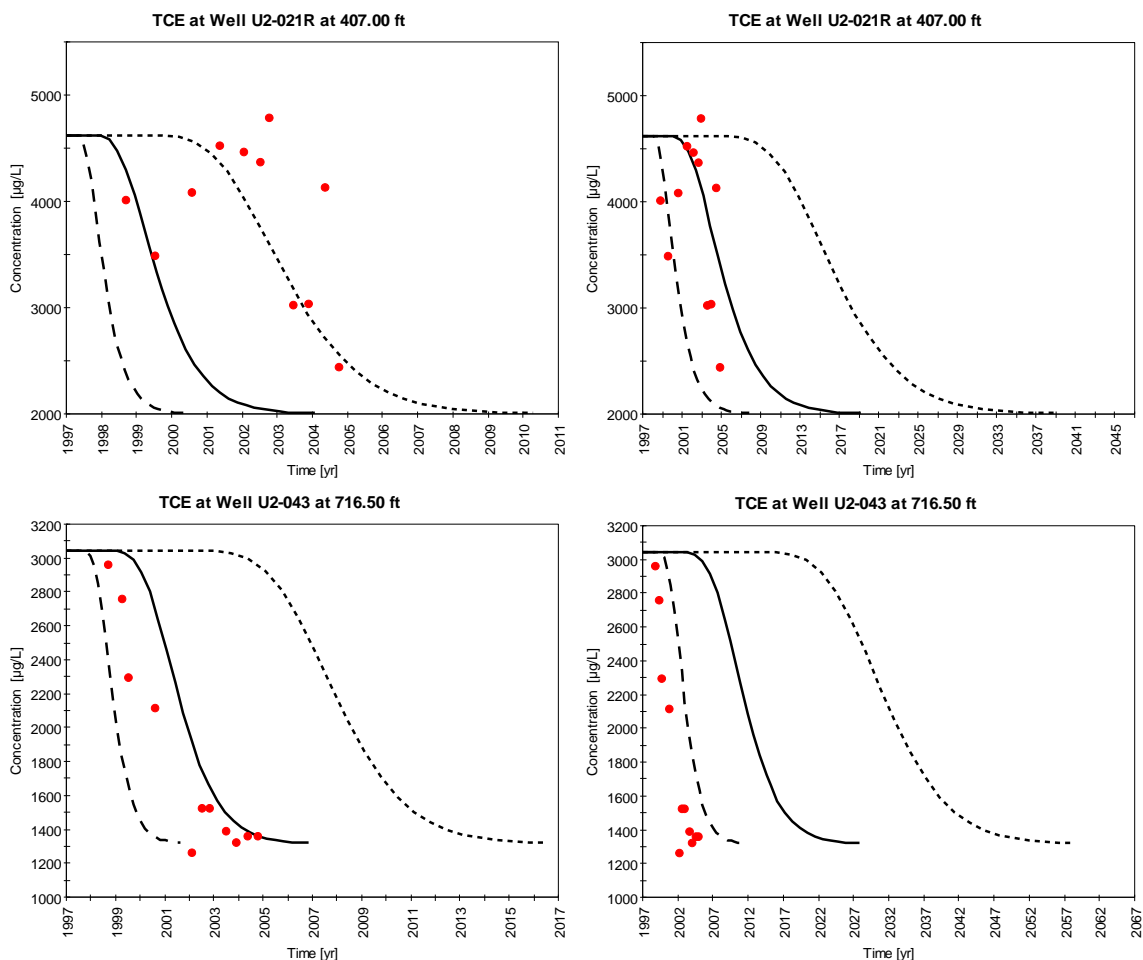
Figure 22. TCE concentration vs. time at wells downgradient of the slurry wall based on hydraulic gradient near the source (left) and further downgradient (right).

4.3.5.   NSB Kings Bay, GA – Site 11

Prior to source treatment, Chapelle and Bradley (1998) estimated the range in the ground-water velocity (0.014 to 0.23 m/d) using Darcy's Law and the range in field-measured hydraulic conductivity, horizontal hydraulic gradient (0.006), and an estimate of effective porosity (0.25). Retardation factors were based on the fraction of organic carbon (0.0019) and published values of the organic carbon partition coefficients. Because PCE rapidly depleted along the ground-water flow path and was absent from the downgradient monitoring wells (KBA-13A and USGS-5) in the pretreatment plume, the range in the estimated composite retardation factor for total chlorinated ethenes is 1.86 to 2.90. The resulting range in the contaminant velocity (0.0050 to 0.12 m/d) shows that the maximum and minimum values vary by a factor of 25.

Figure 23 shows a comparison of observed data at KBA-13A (L = 49 m) with two sets of solutions for the reduction in the total chlorinated ethene concentration versus time; one solution set represents the maximum estimated ground-water velocity (0.23 m/d) using the range of retardation factors (1.89-2.90) and the other represents the initial minimum estimated contaminant velocity range. Results using the initial estimated input parameters show an underestimate of the actual concentration time trend with the best match occurring with the minimum contaminant velocity.
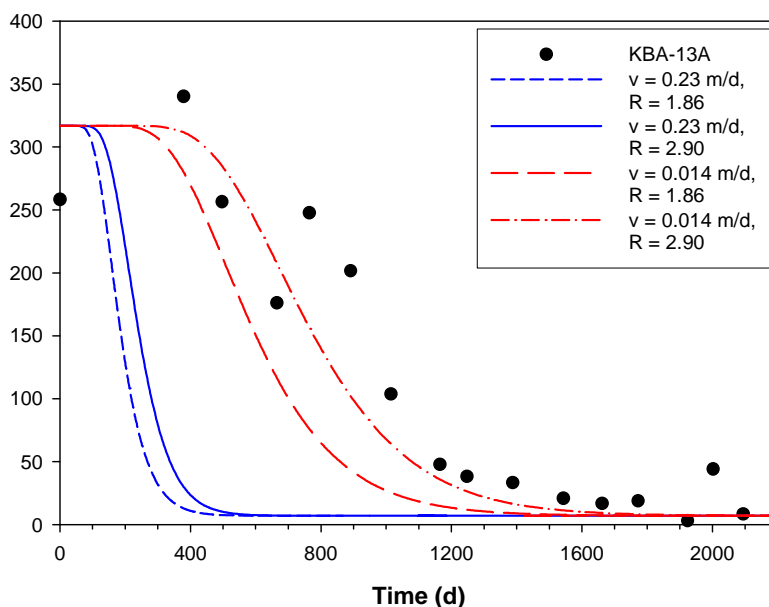
Figure 23. Observed (circles) and predicted total chlorinated ethene concentrations showing the full range of ground-water velocity and retardation factor values based on initial estimates made prior to the source zone treatment.

A tracer-based value of the ground-water velocity is obtained from the breakthrough curve in the sulfate concentration at KBA-13A presented in Chapelle et al. (2005). A pulse of sulfate was

observed in several observation wells resulting from the use of ferrous sulfate with the Fenton's reagent in the source zone and subsequent transport with the natural gradient. The resulting velocity (0.055 m/d) is simply the travel distance between KBA-34 and KBA-13A divided by the travel time (895 d) to the peak sulfate concentration. The results using the tracer-based velocity estimate in Figure 24 show improved agreement between the observed and calculated concentration trend when compared to the initial estimates. However, an improved velocity estimate is only available when the 6-yr monitoring program is approximately 40% complete because the sulfate breakthrough at KBA-13A was not sufficiently ahead of the decrease in the concentration of total chlorinated ethenes to allow an earlier updated prediction. For the tracer-based velocity the minimum value of RMS (30) is achieved for a retardation factor of 2.28.
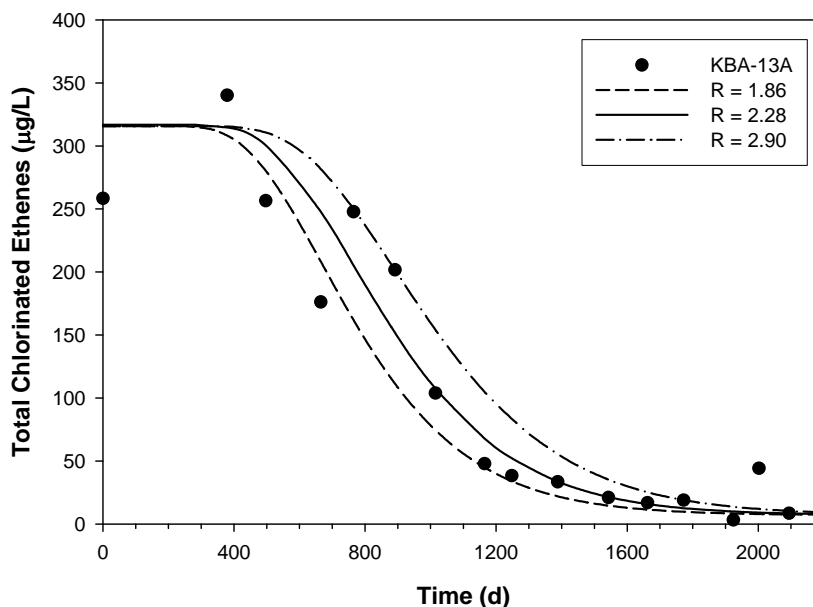
Figure 24. Observed and NAS-predicted total chlorinated ethene concentrations using ground-water velocity ($v = 0.055$ m/d) determined from the tracer breakthrough and the range of retardation factors, including the case ($R = 2.28$) where the error is minimized.

4.3.6.   NAS Cecil Field, FL – Site 3

Estimates of TND in the source area were evaluated for a range of values for contaminant mass and transport velocities. The first set of applications (Figure 25) relates historical concentration data near the source area (CEF-3-13S) to a range of mass estimates at the average seepage velocity (18 ft/yr). The last set of outputs (Figure 26) reflects the sensitivity to the range of seepage velocities (11 ft/yr for minimum velocity and 33 ft/yr for maximum velocity) of the contaminants relative to historical data.
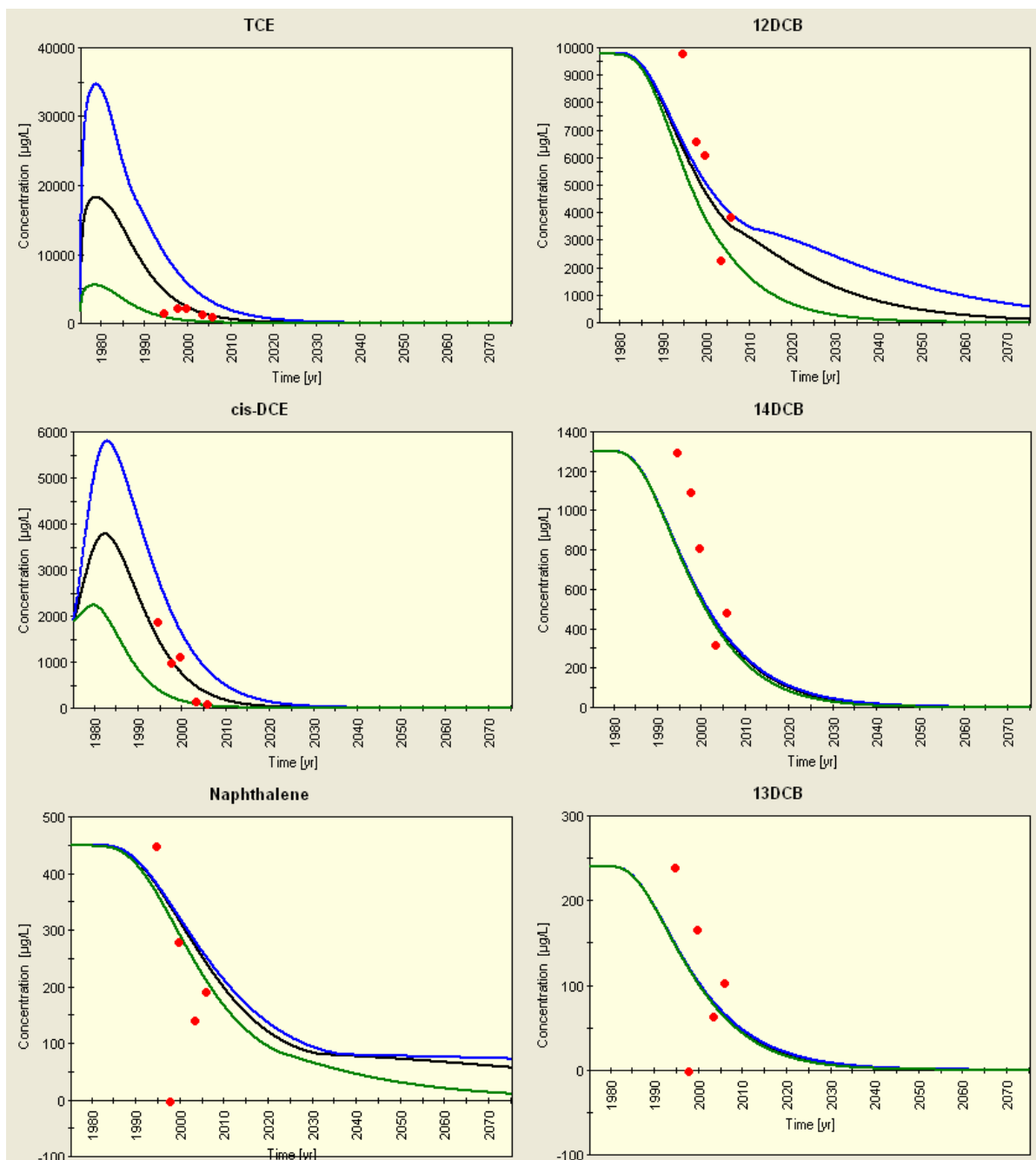
Figure 25. Observed versus NAS-simulated concentrations in the source zone for three source mass estimates.

These results suggest that the VOC concentration trends appear to be most sensitive to estimates of mass during the early stages of NAPL dissolution. During these periods the more soluble compounds elute early and a more pronounced peak is observed in the plume concentrations. The predicted late term behavior of the plume for each estimate of mass begins to reach similar

values around the year 2025. For TCE, the average mass (5000 kg) estimate appears to track the observed data (upper left) near the base of the predicted peak of contaminant concentrations. The degradation product, cis-1,2 DCE, follows the shape of the curve (middle left) initially but the last two observed data points are noticeably lower than the predicted values. These last two data points represent the source area after sparging.
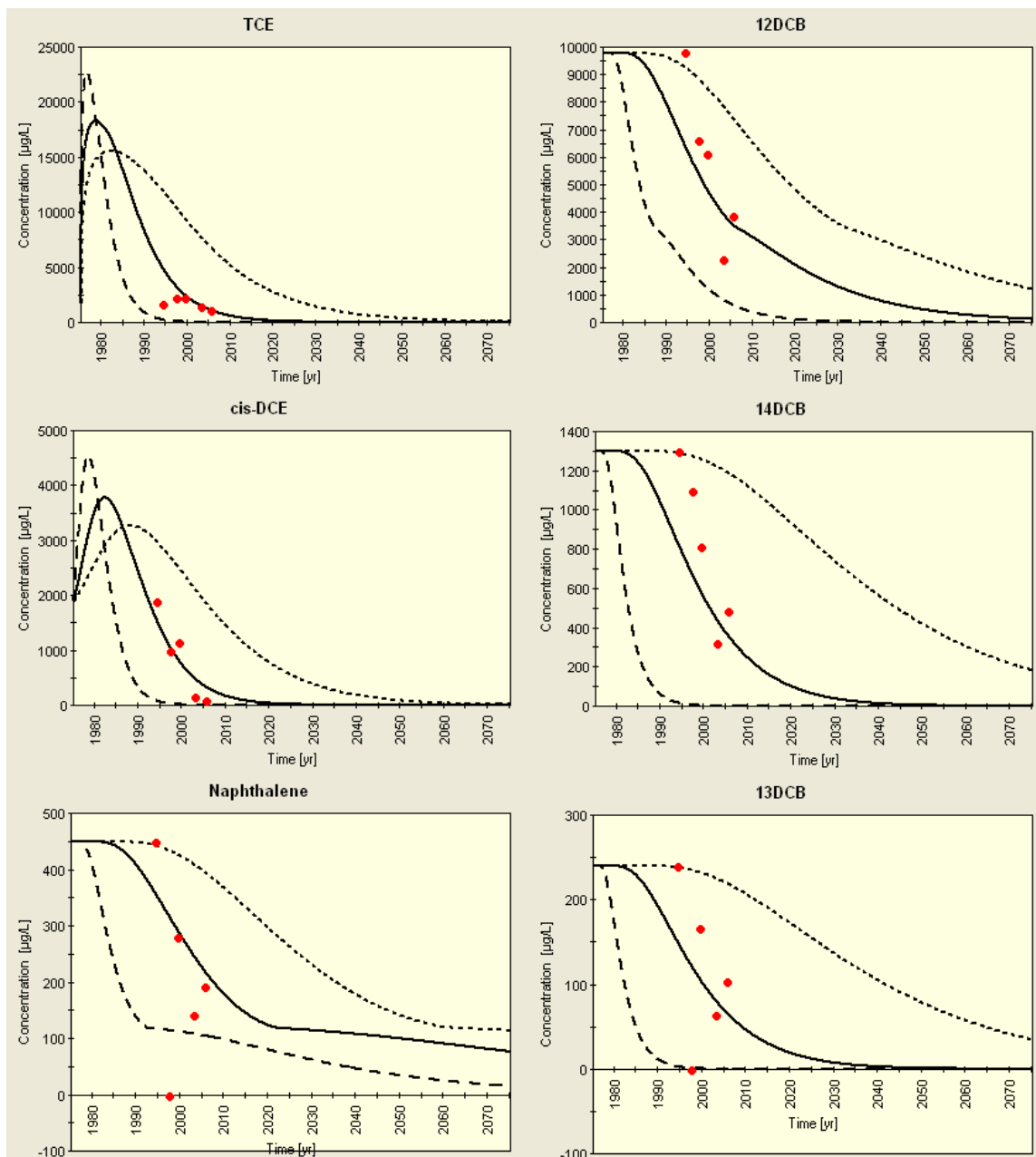
Figure 26. Observed versus NAS-simulated concentrations in the source zone for three velocity estimates.

Because the observed data more closely follows the average estimate (5000 kg) of mass for both VOCs and SVOCs, this value was used to estimate the TND. The potential range of transport velocities predicts a wide range of values that encompasses the observed data (Figure 26). This is partially related to the values that ranged an order of magnitude for the fraction of organic carbon. The average estimate of mass and velocities were used as the basis for the Cost Assessment.

4.3.7.   NAS Pensacola, FL – WWTP

Concentrations of total chlorinated benzenes, benzene, and 1-3 dichlorobenzene over time in ground-water produced from Well SMW-8 following source area treatment (ORC) in 2001 are shown in Figure 27 (top, middle, and bottom, respectively). For the case of total chlorinated benzenes, the observed data generally fall within the uncertainty envelope of the predicted time of remediation curves. However, considerable variability between prediction and observation are evident. Similar comparisons between predicted and observed concentration trends are found with other contaminants as well.

A comparison of predicted and observed benzene concentrations versus time plot of benzene shows a different pattern than observed for total chlorinated benzenes. In particular, the observed data decrease systematically slower than indicated by the simulation. Concentrations of 1-3 dichlorobenzene in well SMW-8, on the other hand, show a rate of decrease greater than indicated by the NAS simulation.

4.3.8.   Alaska DOT&PF – USGS (Peger Road) Site

In 2003, the Alaska DEC initiated an experimental study of chloroethene biodegradation the Peger road site. Briefly, aquifer sediments from the site were collected, returned to the laboratory, and amended with several carbon-14 labeled chloroethene compounds, including TCE (Bradley and Chapelle, 2004). These experiments provide an opportunity to compare biodegradation rates estimated by NAS with laboratory-measured rates. The laboratory-derived rates were estimated in two ways: (1) rates were estimated by substrate loss (SL) of ^{14}C-TCE in the experimental vials over time and (2) rates were estimated by daughter product production (DPP) of ^{14}C-TCE. Experiments were conducted with sediments collected from near the source are (Well MW98-10) and in the downgradient part of the plume (Well N4). The results of this comparison are shown in Table 7. Concentrations of TCE and redox conditions along the centerline of the plume are shown in Figure 28. TCE concentration decreases indicate relatively low rates of biodegradation associated with oxic conditions near the source area, and continued low biodegradation rates in the Fe(III)-reducing conditions downgradient of the source area.
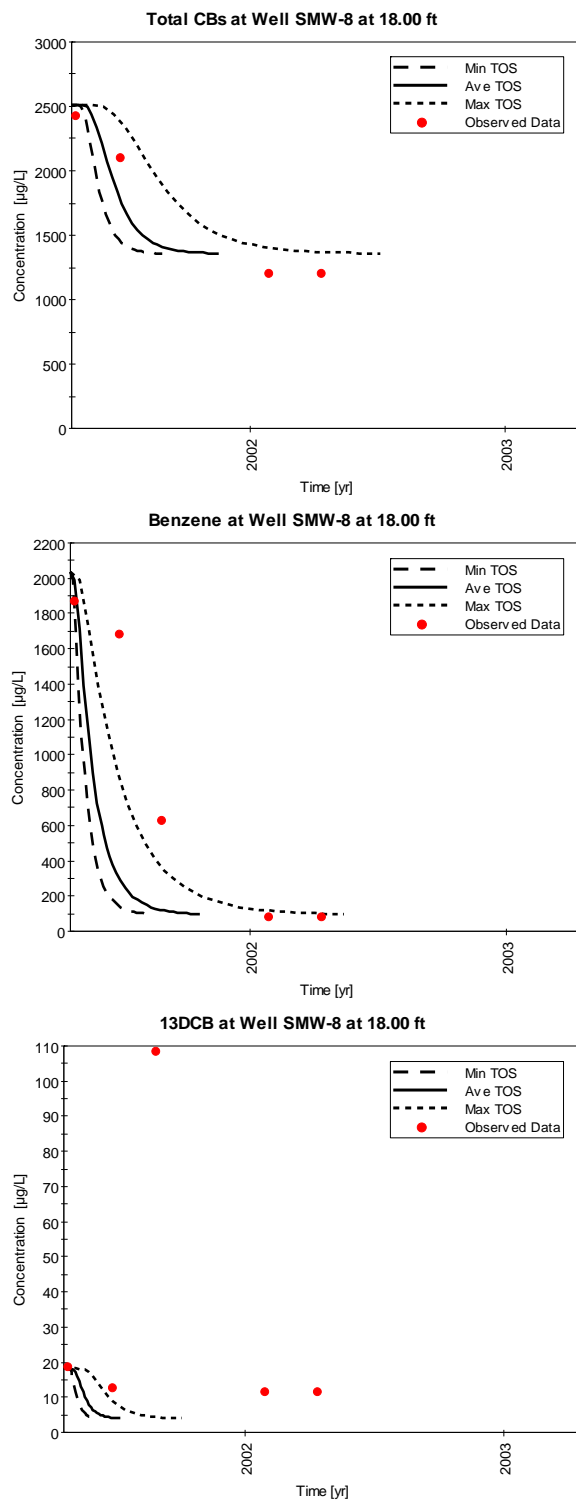
Figure 27. Concentrations of total chlorinated benzenes (top), benzene (middle), and 1-3 dichlorobenzene (bottom) over time at well SMW-8 following ORC treatment of the source.

Experimental rate constant measurement indicates very slow biodegradation in this system. These are some of the lowest TCE biodegradation rates measured in the laboratory, and are possible only because of the extreme sensitivity of the carbon-14 methodology used. The NAS-derived biodegradation rates are also very low, but they are consistently an order of magnitude higher than the laboratory-derived rate constants. The most appropriate conclusion that can be made from this comparison is that both methods indicate very low rates of TCE biodegradation in this system. The fact that the laboratory rates were lower than NAS-derived rates may or may not be meaningful. The NAS-derived rates reflect in situ conditions, and it is possible that sample handling and experimental manipulation decreased laboratory rates. Alternatively, the hydrologic uncertainties associated with observation well data may artificially increase NAS-derived rates. In either case, both experimental and NAS methods indicate low biodegradation rates at this site, which is consistent with the relatively oxidized nature of this system.

Table 7. Comparison of Experimentally-Derived and NAS-Derived Rate Constants

Sediment (NAS redox zone)	Experimental Method	Experimental ^{14}C-TCE dechlorination rate (d^{-1})	NAS-derived TCE biodegradation rate (d^{-1})
MW 98-10 (aerobic zone)	SL	0.0001 ± 0.00015	Max 0.0247 Ave 0.0082 Min 0.0021
MW 98-10 (aerobic zone)	DPP	0.00015 ± 0.00006	
N3 (ferrogenic zone)	SL	0.00005 ± 0.00004	Max 0.026 Ave 0.0087 Min 0.0022
N3 (ferrogenic zone)	DPP	0.00015 ± 0.00008	
SL = substrate loss DPP = daughter product production			

The results of NAS simulations of TOS immediately downgradient of the source area at Well MW98-17 (distance = 140 ft) are shown in Figure 29. As in all TOS simulations, the assumption is made that a source-area removal action has been undertaken (in this case, in 1998), and that a plume of remediated water is moving through the observation well. The simulated concentration profile curves represent the expected behavior of the plume for the case of minimum, average, and maximum rates of ground-water flow. Also shown on Fig. 29 are the observed data points measured at the site.

Inspection of Fig. 29 indicates that observed TCE concentrations at Well MW98-10 clearly falls outside the envelope of uncertainty for maximum and minimum rates of ground-water flow. This behavior is expected because no source-area removal was undertaken in 1998 as assumed by the simulation. Interestingly, however, the overall shape of the observed TCE concentration decline is not dissimilar to the predicted behavior assuming the lowest rates of ground-water flow. One interpretation of these results is that a source of TCE remains in or near the source area, but that this source is being depleted over time. Furthermore, this depletion is rapid enough that the observed behavior of the plume mimics a source-removal action.
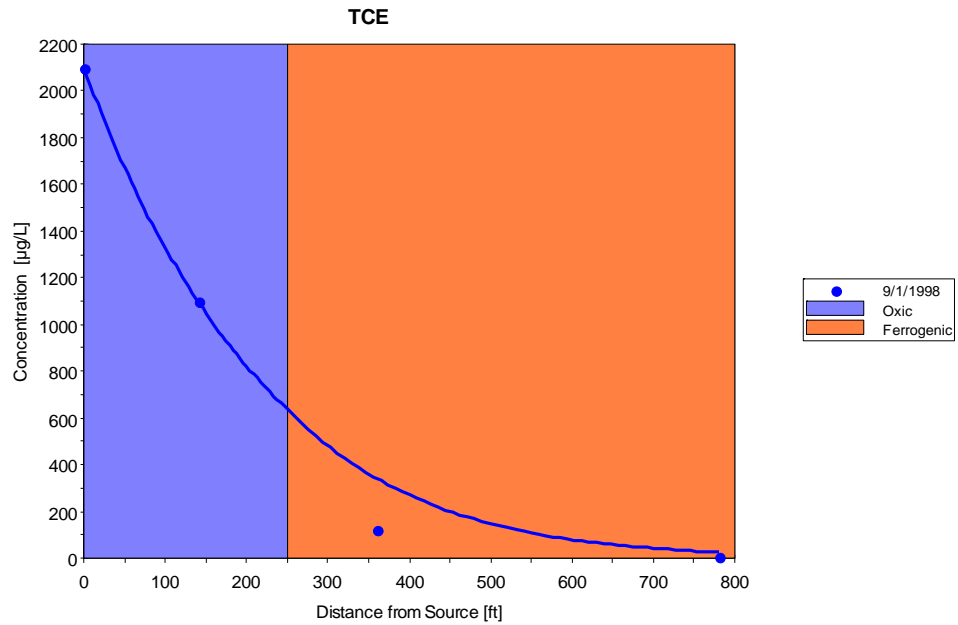
Figure 28. TCE plume centerline concentration profile and redox conditions.
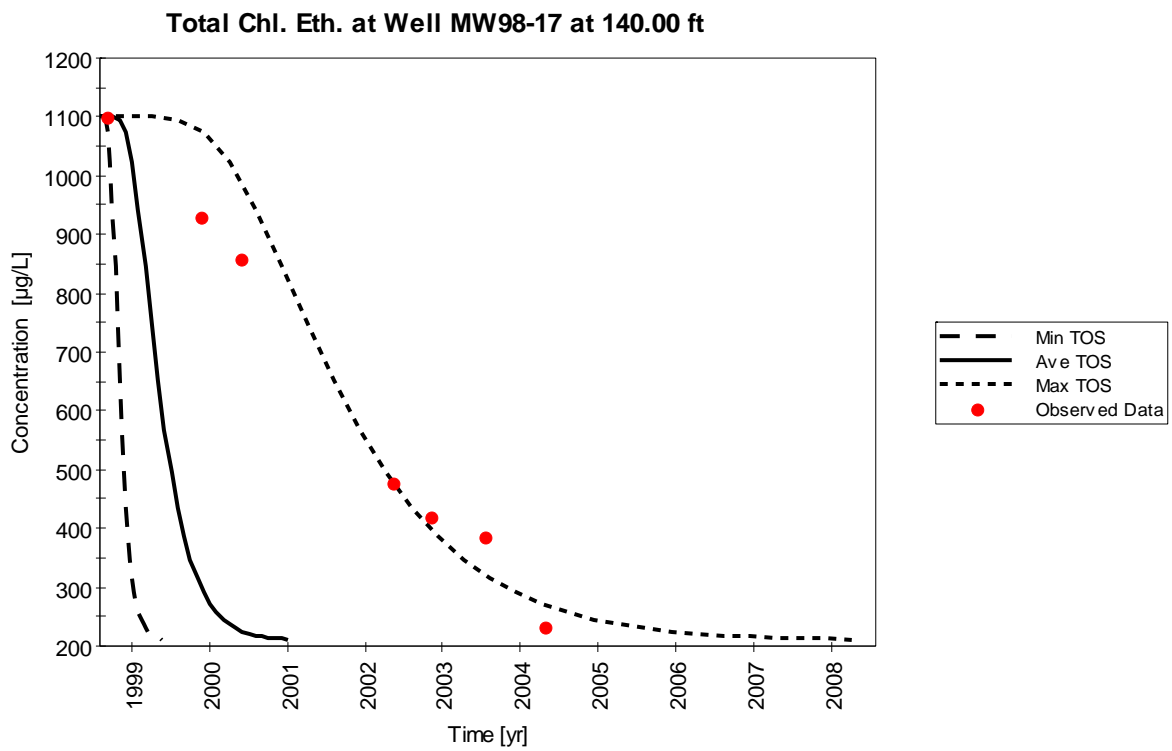
Figure 29. NAS simulation of time of stabilization at well MW98-17.

4.4. Overall Performance Assessment

4.4.1. Accuracy

The DOS/TOS feature of NAS was tested at 5 sites and the TND feature was tested at the remaining 3 test sites (Table 6). Overall, the DOS/TOS feature was satisfactory in meeting quantitative and qualitative performance objectives based on the match between NAS and the data inflection points and concentration versus time slopes, respectively. The other quantitative performance objective, time of breakthrough, was also satisfactory except at the Seneca site, where data variability prevented a credible determination of breakthrough. Factors affecting the degree of accuracy were reflected in the uncertainty associated with the contaminant velocity estimates and source characteristics (width and concentration) following remediation.

It is important to restate that site applications using the DOS/TOS feature was not a curve-fitting exercise. NAS self-calibrates a steady-state solution to the pre-remediation plume concentration data and then calculates concentration versus time at downgradient monitoring wells using the field-measured source concentration following remediation. The best matches between the observed and simulated concentrations, including inflection points, were achieved at the monitoring wells closest to the source (travel distances ranging from 18 to 407 ft with an average of 185 ft from source). In general, less accurate results were observed at monitoring wells located further downgradient from the source. As was noted in Section 4.3.1 (Seneca), decrease in the source width following remediation can reposition the plume centerline and potentially reduce the concentration at some monitoring wells. NAS only accounts for a reduction in the contaminant concentration leaving the source zone and does not account for changes in the source width following remediation. The issue is amplified at sites where time fluctuations in the direction and magnitude of the ground-water velocity impact plume concentrations. Time fluctuations in concentration can be expected in situations where the contaminant mass flux "misses" the well if the direction of ground-water flow changes seasonally. The most accurate results were observed at NSB Kings Bay where the ground-water velocity was calculated based on tracer test data. These findings suggest that accurate determinations of the ground-water velocity and sorption parameters are required for improved accuracy of TOS following source zone remediation at all sites.

Results of the TND simulations show that NAS was capable of simulating the dissolution and dissipation of individual NAPL components at the remaining three sites listed in Table 6. In these applications, a match between observed and simulated concentrations at a source area monitoring wells was achieved based on reasonable estimates of the mass and dimensions of the source zone along with composition of the NAPL. This finding suggests that at some sites, knowledge of NAPL source complexities (e.g., interfacial area) is not required for a reasonably accurate estimate of TOR. However, the dependency of concentration versus time results on source zone mass and length along with NAPL composition suggests that source characterization methods have the potential to reduce the uncertainty associated with source dissipation calculations using NAS. The NAS simulation results also demonstrate the value and efficiency of refining TND predictions using post-remediation data.

4.4.2. Versatility

Site hydrogeology did not appear to be a factor in the performance of NAS. Four of the sites were located in coastal plain regions, and the other 4 sites reflect more diverse and complex hydrogeologic settings (Figure 4). For the latter set of sites, a reasonable match between observed data and NAS simulation results of TOS and TND was obtained. Similarly, the mode of source remediation (Table 6) was not a factor in the performance of NAS. However, as was noted in the Section 4.4.1., reduction of the source width can affect post-remediation concentration data and represents an inconsistency with the DOS/TOS feature. Even for the case of a containment wall, the NAS application resulted in an adequate match with observed data at monitoring wells located a sufficient distance away from the wall where the groundwater flow returned to a natural condition.

4.4.3. Reliability

No significant reliability problems were encountered in the implementation of NAS at all eight sites. NAS version 2.2.0 was utilized for the site applications.

4.4.4. Applicability

NAS was designed to be used as a stand-alone screening tool but can be applied to sites as a either a precursor to a comprehensive (numerical) solute transport modeling investigation or as a follow-up to previous modeling study. One finding of this demonstration was that NAS proved to be applicable to all eight sites, independent of hydrogeology, contaminants, characteristics of the source zone, or ERA. Therefore, the simplifying assumptions associated with the analytical solutions and the numerical source zone model do not appear to render NAS ineffective but, in fact, demonstrate the applicability and utility of NAS to a wide range of contaminated sites. In contrast, comprehensive three-dimensional numerical models that are constructed to simulate the complexities of a groundwater system and features of a plume often are subject to limited data and may include unrealistic boundary conditions that do not honor the actual field conditions. One example is the source term in many models (e.g., RT3D) is not based on the concept of mass balance. In contrast, the source model in NAS implements the NAPL Dissolution Package of SEAM3D in which mass is conserved for all components in the aqueous, solid and NAPL phases. The results of this demonstration strongly suggest that because NAS is based on sound science, it can serve as an effective tool for decision-making, data analysis, and cost optimization at a wide range contaminated sites and is not limited to a small subset of "simple sites" because of its simplicity.

5. Cost Assessment

5.1. Cost Reporting

The NAS software is used to estimate the time in which remedial objectives will be met. Once this timeframe is established, the cost to monitor the site can be estimated. Typical costs associated with a long-term performance monitoring program include the cost of sampling and analysis of wells and preparation of annual reports regarding the progress of remediation at the site. Often, long term monitoring programs incorporate more frequent sampling at the beginning of the monitoring program and a less frequent sampling as trends become established and seasonal impacts are understood. At sites where source remediation is combined with MNA, the cost of implementing source ERA is included. For this demonstration the estimated cost was determined to sample the number of wells at the NAS Cecil Field site until the estimated time to reach remedial objectives was met. The basis for the cost estimate is summarized in Table 8.

Table 8. Basis for NAS Cecil Field Life Cycle Cost Estimates

Cost Factor	Variables
Number of Wells in Sampling Program	Optimized Sampling Program?
Frequency of Sampling	Optimized Sampling Program?
Sample Collection	Geographic Labor Rates and Well Characteristics
Field and Laboratory Analysis	Fixed Base Lab. and Field Portable Kits
Time to meet remedial objectives	Estimated Within a Range by NAS
Source Zone Removal	Yes/No?
Annual Reporting	Geographic Labor Rates

NAS may be used as part of a RI/FS or in a post-ROD analysis of a site where MNA with or without source remediation is the selected remedy. Under both of these scenarios the time and cost to build a comprehensive flow and transport numerical model can require significant effort including the additional cost associated with collecting the required field data.

For this demonstration the estimated cost to implement NAS was estimated and compared to the estimated cost associated with implementing a comprehensive flow and transport model to evaluate MNA. The analysis compares the cost of using the two technologies early in the RI/FS with the same data availability. For implementing a comprehensive model, the general tasks identified include development of a modeling plan, construction of both the flow and transport model, model implementation (including calibration, sensitivity analysis, and predictive simulation for TOR), and reporting. NAS is designed to eliminate the labor-intensive tasks of constructing and calibrating both the flow and transport models. In the addition, because NAS is a screening tool, the labor requirement for the remaining tasks is significantly less for NAS analysis relative to a comprehensive model.

5.2.   Cost Analysis

5.2.1.   Life Cycle Cost Analysis

An estimate of the life cycle costs of monitoring associated with TND for the current MNA remedy at NAS Cecil Field (Site 3) was developed in conjunction with NAS TOR estimates. The present cost of semi-annual monitoring for VOC's, SVOC's and geochemical parameters at eleven monitoring wells is shown in Table 9. The cost of preparing an annual report is $100,000. The net present value of long term monitoring at Site 3 is estimated in Table 9 using both the estimated TND for TCE (43 years) and naphthalene (>69 years) to achieve NFA criteria. The net present value for monitoring over this period of time is at least $2,333,029.

The accuracy of these cost estimates is largely dependent on the TOR and monitoring requirements. As a result of the high TOR estimates and associated life cycle costs, as well as the decreased rates of natural attenuation of the chloroethenes in the source zone resulting from air sparging in this area of the plume, additional optimization at Site 3 is recommended.

Table 9. Estimated Cost for MNA at Site 3.

Description	Annual Costs
Reporting and Project Management	$100,000
Total (TCE)[1]	$2,037,079[3]
Total (Naphthalene)[2]	$2,333,029[3]
[1]TND = 43 years	
[2]TND = >69 years	
[3]assuming a 4 percent return on investment	

This illustrative example of the potential costs for a MNA-based remedy, and the dependence on accurate TOR estimates, demonstrates the potential value of the NAS model in making site management decisions. The following section discusses the costs for this type of modeling effort, and compares those costs to the cost for the most common alternative approach to estimating TOR; the use of comprehensive numerical flow and transport models.

5.2.2.   Implementation Cost Analysis

An estimate of the cost to implement a model in conjunction with the scope of work associated with the RI/FS is highly site specific. Comprehensive models for ground-water flow and contaminant transport are often used to evaluate a range of remedial strategies. Direct cost comparison to previously implemented sites (e.g., NAES Lakehurst) are problematic, because the work associated with implementation of models is typically buried inside of the total cost of conducting a FS at a site.

Table 10 provides a comparison of the two methods. Although NAS is designed to be used by personnel who may not have adequate education and/or training to implement a comprehensive model, the same hourly rate ($150/hr) is used for this comparison. The development of a modeling plan entails evaluation of site data (hydrogeologic, contaminant, and redox indicator data), description of a conceptual model, and detailed plans for construction of the numerical model and parameter estimation. The latter task is not required for NAS but constitutes a significant labor cost for a comprehensive model. As reflected in the costs shown in Table 10, less documentation is required for NAS. To implement a flow and transport model at the same site, larger time requirements are largely due to the efficiency of NAS and the difficulty in constructing and calibrating a fully 3D (or even 2D) numerical model. In addition, the reporting requirements are substantially greater for documenting the comprehensive approach.

Table 10. Estimated Costs for Performing a TOR Analysis Using NAS or a Comprehensive Numerical Model at a Hypothetical Site.

Task Description	NAS	Comprehensive Model
Modeling Plan	$6,000	$31,500
Model Construction	$1,200	$12,000
Calibration and Sensitivity Analysis	$2,400	$24,000
TOR Simulation	$3,600	$22,500
Reporting	$6,000	$18,000
Total	$19,200	$108,000

The ratio of the estimated cost of using NAS compared to the cost of using a comprehensive model is equal to the ratio of the estimated hours (5.6:1) to complete the analysis ($19,200 and $108,000, respectively). Note that the costs shown in this comparison do not account for establishment of a contract, management of this contract, or contracting rates and fees. It is reasonable to assume that the sum of these costs will be larger for an investigation using a comprehensive model. In addition, it is reasonable to assume that level of oversight by both a senior technical expert and regulating agencies will be greater in this case relative to NAS, resulting in higher costs for the use of a comprehensive model. Thus, the costs provided in Table 10 do not include the total costs involved, and these additional costs are likely to be considerably higher when using comprehensive numerical models compared to using NAS.

Another cost-saving feature of NAS is the number of monitoring wells required for TOR analysis. Because NAS only requires data from the approximate plume centerline, costs associated with sample collection and analysis can be substantially reduced using NAS. As a means to compare total cost savings, two hypothetical sites are considered; the "small site" and the "large site". The number of monitoring wells needed to reasonably represent the plume centerline varies between the small (7) and large (11) sites. These assumptions are based in part on the NAS site applications described in this report. Per sample costs of a one-time event for laboratory and field analysis of groundwater constituents used for this comparison are $300 for quantifying contaminant concentrations and $150 for redox indicator data.

Table 11 summarizes the total cost for each case using the two modeling approaches. The results show that an overall per site cost savings from $94,650 to $126,030 can be realized by using NAS as the modeling approach. Although cost savings at any given site will vary, the results suggest that considerable savings can be achieved when determining TOR using NAS relative to comprehensive modeling due to the lower data requirements associated with NAS implementation.

Table 11. Cost Comparison and Savings for Two Hypothetical Sites of Differing Size.

Site	Samples	Conventional Analytical[1]	Total[2, 3]	Samples	NASv2 Analytical[1]	Total[2, 3]	Cost Savings Analytical	Total
Small	20	$9,000	$117,000	7	$3,150	$22,350	$5,850	$94,650
Large	50	$22,500	$152,100	11	$4,950	$26,070	$17,550	$126,030

[1]Analytical sampling and analysis costs = $300/well for contaminants and $150/well for redox indicators
[2]Total costs = Sum of analytical and modeling (Table 7)
[3]Costs increase for modeling large sites = 20% and 10% using conventional models and NAS, respectively

A cost comparison illustrating potential cost savings achieved at multiple sites over a 5-year period is shown in Figure 30 where it is assumed that 75% of the NAS applications take place at small sites. In this scenario, one site per month is modeled using NAS in year 1. In years 2 and 3, the number of sites increases to two and four per month, respectively, as a result of technology transfer efforts focused on the use and benefits of NAS. In years 4 and 5, the number of sites evaluated using NAS becomes five per month, resulting in the total of 204 sites evaluated using NAS. The cumulative five-year cost savings to DoD by implementing NAS relative to a comprehensive model at contaminated sites for the purpose of estimating TOR is $20,900,000. Because this comparison does not factor in a rate of savings over time and does not include the potential cost saving for implementing a MNA-based strategy, this total may underestimate the true savings.
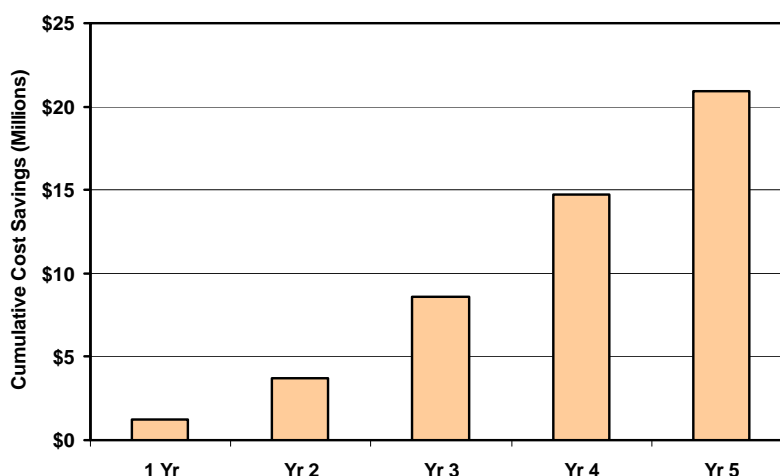
Figure 30. Cost savings using NAS over a 5-year period, beginning with 12 sites in Year 1, 24 sites in Year 2, and 48 sites in Year 3-5. The ratio of small sites to large sites is 4:1.

6. Implementation Issues

6.1.   Environmental Checklist

Not applicable.

6.2.   Other Regulatory Issues

Following approval for dissemination, the Final Report will be released and sent to key individuals within the regulatory community (e.g., EPA, ITRC, etc.). In addition, the results of the site applications will be presented to state regulators at a planned series of short courses and seminars. We will also utilize recommendations from ESTCP, ITRC, and others to help us determine the most appropriate ITRC group and vehicle for interaction with the general public.

6.3.   End-User Issues

Stakeholder buy-in is evident by the support provided by Navy Engineering Field Divisions. This is exemplified by the recently funded NAS upgrade to allow for incorporation of a source removal term. Earlier versions of NAS have been the subject of Navy supported conference presentations (e.g., the annual RPM Conference in Port Hueneme) and a RITS course module. End-user concerns, reservations, and buy-in factors all point to the remedial project managers' (RPM) willingness to utilize the NAS approach versus a more comprehensive modeling effort. Concerns with implementation have been addressed through the NAS site applications using feedback from users during this demonstration.

7. References

ABB-ES. 1996. Remedial Investigation, Operable Unit 8, Site 3, Naval Air Station Cecil Field, Jacksonville, Florida. Prepared for Southern Division, Naval Facilities Engineering Command.

ABB-ES. 1997. Feasibility Study, Operable Unit 8, Site 3, Naval Air Station Cecil Field, Jacksonville, Florida. Prepared for Southern Division, Naval Facilities Engineering Command.

Air Force Center for Environmental Excellence. 2003. Conceptual Model Update for Operable Unit 2 Source Zone: Hill Air Force Base, Utah.

Alaska Department of Environmental Conservation. 2005. ADOT&PF Peger Road Maintenance Facility, Fairbanks, Alaska.

Bradley, P.M., and F.H. Chapelle. 1996. Anaerobic mineralization of vinyl chloride in Fe (III)-reducing aquifer sediments. Environ. Sci. Technology. 30:2084-2086.

Chapelle, F.H., and P.M. Bradley. 1998. Selecting remediation goals by assessing the natural attenuation capacity of groundwater systems. *Bioremediation Journal*, 2(3&4): 227-238.

Chapelle, F.H., M.A. Widdowson, J.S. Brauner, E. Mendez, and C.C. Casey. 2003. Methodology for estimating times of remediation associated with monitored natural attenuation, USGS Water Resource Investigation Report 03-4057, 51 p.

Chapelle, F.H., P.M. Bradley, and C.C. Casey. 2005. Behavior of a chlorinated ethene plume following source-area treatment with Fenten's reagent. *Ground-water Monitoring and Remediation*, 25(2): 131-141.

Dames and Moore. 1999. Final Report – Groundwater Natural Restoration Study, Areas I and J. Contract Number N62472-90-D-1298.

Ensafe/Allen and Hoshall. 1995. Final remedial investigation report, Naval Air Station Pensacola, Operable Unit 10 and site 13. Ensafe/Allen and Hoshall, Memphis, Tennessee.

EnSafe/Allen & Hoshall. 1997. Final Record of Decision Operable Unit 10, NAS Pensacola, Pensacola, Florida. EnSafe/Allen & Hoshall, Memphis, Tennessee.

Halford, K.J. 1996. Ground-Water Flow in the Surficial Aquifer System and Potential Movement of Contaminants from Selected Waste-Disposal Sites at Cecil Field Naval Air Station, Jacksonville, Florida. United States Geological Survey. Administrative Release.

Mendez, E., M. Widdowson, S. Brauner, F. Chapelle and C. Casey. 2004. Natural Attenuation Software (NAS): A computer program for estimating remediation times of contaminated groundwater, In: G. Latini, G. Passerini, and C. Brebbia (eds.), *Development and Application of Computer Techniques to Environmental Studies X (ENVIROSOFT 2004)*.

National Research Council. 2004. *Contaminants in the Subsurface: Source Zone Assessment and Remediation*. National Academic Press., Washington, D.C., 294 p.

Parsons Engineering. 2004. Final Record of Decision for Ash Landfill at Seneca Army Depot Activity, Romulus, NY (Contract Number: DACA87-95-D-0031).

U.S. Department of Energy. 2003. Natural and Passive Remediation of Chlorinated Solvents: Critical Evaluation of Science and Technology Targets, WSRC-TR-2003-00328, U. S. Department of Energy, Office of Scientific and Technical Information, Oak Ridge TN.

U.S. Environmental Protection Agency. 1996. Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground-water (EPA/540/R-97/504).

U.S. Environmental Protection Agency. 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground-water (EPA/600/R-98-128).

U.S. Environmental Protection Agency. 1999. Final OSWER Monitored Natural Attenuation Policy (OSWER Directive 9200.4-17P). Office of Solid Waste and Emergency Response, Washington, DC.

U.S. Environmental Protection Agency. 2001. Handbook of Groundwater Protection and Cleanup Policies for RCRA Corrective Action (EPA/530/R-01/015).

U.S. Environmental Protection Agency. 2004. Textron Realty Operations, Inc. Fact Sheet.

U.S. Geological Survey. 1999. Natural Attenuation of Chlorinated Ethenes and Chlorinated Benzenes, Wastewater Treatment Plant, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina.

U.S. Geological Survey. 2000. Delineation of a Benzene/Chlorobenzene Hotspot Related to Sludge Drying Beds at the WWTP, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina.

U.S. Geological Survey. 2005. Chloroethene biodegradation potential in the "lower" contaminant plume, River Terrace RV Park, Soldotna, Alaska, U.S. Geological Survey Open-File Report 2004-1427.

Waddill, D.W. and M.A. Widdowson. 1998. Three-Dimensional Model for Subsurface Transport and Biodegradation. *ASCE J. of Environmental Engineering*. 124(4): 336-344.

Waddill, D.W. and M.A. Widdowson. 2000. SEAM3D: A numerical model for three-dimensional solute transport and sequential electron acceptor-based bioremediation in groundwater, ERDC/EL TR-00-X, U.S. Army Engineer Research and Development Center, Vicksburg, MS, 89 pp.

Widdowson, M.A. 2004. Modeling natural attenuation of chlorinated ethenes under spatially-varying redox conditions, *Biodegradation*, 15, 435-451.

Wiedemeier, T.H., Rifai, H.S., Newell, C.J., and Wilson, J.T. 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. John Wiley & Sons, Inc., New York, 617 p.

Yager, R.M. 2002. Simulated Transport and Biodegradation of Chlorinated Ethenes in a Fractured Dolomite Aquifer Near Niagara Falls, New York: U.S. Geological Survey Water-Resources Investigations Report 00-4275, 55 p.

Figure Number	Reference
4	www.nationalatlas.gov
5	Parsons Engineering. 2004. Final Record of Decision for Ash Landfill at Seneca Army Depot Activity, Romulus, NY (Contract Number: DACA87-95-D-0031).
8	Dames and Moore. 1999. Final Report – Groundwater Natural Restoration Study, Areas I and J. Contract Number N62472-90-D-1298.
9	Air Force Center for Environmental Excellence. 2003. Conceptual Model Update for Operable Unit 2 Source Zone: Hill Air Force Base, Utah.
11	Chapelle, F.H., P.M. Bradley, and C.C. Casey. 2005. Behavior of a chlorinated ethene plume following source-area treatment with Fenten's reagent. *Ground Water Monitoring and Remediation*, 25(2): 131-141.
12	NAVFAC report. 2006.
13	U.S. Geological Survey. 1999. Natural Attenuation of Chlorinated Ethenes and Chlorinated Benzenes, Wastewater Treatment Plant, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina.
14	U.S. Geological Survey. 2005. Chloroethene biodegradation potential in the "lower" contaminant plume, River Terrace RV Park, Soldotna, Alaska, U.S. Geological Survey Open-File Report 2004-1427.
15	Alaska Department of Environmental Conservation. 2005. ADOT&PF Peger Road Maintenance Facility, Fairbanks, Alaska.
App. A (Seneca); 1	Parsons Engineering. 2004. Final Record of Decision for Ash Landfill at Seneca Army Depot Activity, Romulus, NY (Contract Number: DACA87-95-D-0031).
App. A (Seneca); 2	Parsons Engineering. 2004. Final Record of Decision for Ash Landfill at Seneca Army Depot Activity, Romulus, NY (Contract Number: DACA87-95-D-0031).
App. B (Niagara); 1	Yager, R.M. 2002. Simulated Transport and Biodegradation of Chlorinated Ethenes in a Fractured Dolomite Aquifer Near Niagara Falls, New York: U.S. Geological Survey Water-Resources Investigations Report 00-4275, 55 p.
App. C (Lakehurst); 1	www.lakehurstnj.org
App. C (Lakehurst); 2	Dames and Moore. 1999. Final Report – Groundwater Natural Restoration Study, Areas I and J. Contract Number N62472-90-D-1298.
App. C (Lakehurst); 3	Dames and Moore. 1999. Final Report – Groundwater Natural Restoration Study, Areas I and J. Contract Number N62472-90-D-1298.
App. C (Lakehurst); 4	Dames and Moore. 1999. Final Report – Groundwater Natural Restoration Study, Areas I and J. Contract Number N62472-90-D-1298.
App. E (Kings Bay); 1	Chapelle, F.H., P.M. Bradley, and C.C. Casey. 2005. Behavior of a chlorinated ethene plume following source-area treatment with Fenten's reagent. *Ground Water Monitoring and Remediation*, 25(2): 131-141.
App. F (Cecil Field); 1	NAVFAC report. 2006.
App. F (Cecil Field); 2	NAVFAC report. 2006.
App. G (Pensacola); 1	U.S. Geological Survey. 1999. Natural Attenuation of Chlorinated Ethenes and Chlorinated Benzenes, Wastewater Treatment Plant, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina.
App. G (Pensacola); 2	U.S. Geological Survey. 1999. Natural Attenuation of Chlorinated Ethenes and Chlorinated Benzenes, Wastewater Treatment Plant, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina.
App. G (Pensacola); 3	U.S. Geological Survey. 2000. Delineation of a Benzene/Chlorobenzene Hotspot Related to Sludge Drying Beds at the WWTP, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina.
App. H (Alaska); 1	Alaska Department of Environmental Conservation. 2005. ADOT&PF Peger Road Maintenance Facility, Fairbanks, Alaska.
App. H (Alaska); 2	Alaska Department of Environmental Conservation. 2005. ADOT&PF Peger Road Maintenance Facility, Fairbanks, Alaska.
App. H (Alaska); 3	*(NAS snapshot)*

8. Points of Contact

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Appendix A: Seneca Army Depot, NY – Ash Landfill

Seneca Army Depot, NY – Ash Landfill

1.0   Test Site

1.1   History of Operations at the Site

The Seneca Army Depot Activity (SEDA) encompasses 10,587 acres and it locates between Seneca and Cayuga Finger lakes, in Romulus New York (Figure 1). The site was acquired by the U.S. Government in 1941 to store and dispose of military explosives. In 2000, the military mission in this area ceased causing the site to close down. The Ash Landfill site is located along the western boundary of the SEDA with an extension of approximately 130 acres (Figure 2). This site, currently abandoned, consisted of an Incinerator Cooling Water Pond, the Ash Landfill, a Non-Combustible Fill Landfill (NCFL), Refuse Burning Pits and a Solid Waste Incinerator Building. The operation at the Ash landfill site was primary focused on eliminating the trash produced at the depot. This task was achieved by first burning the solid waste using the refuse burning pits (between 1941 and 1974) or using the incinerator building (between 1974 and 1979). The ashes were stored in the Incinerator Cooling Water Pond until filled to be later transported to the Ash Landfill. Those items that could not be burned were discarded at the NCFL. The Ash Landfill site was active until May 8, 1979, when a fire destroyed the incinerator building.
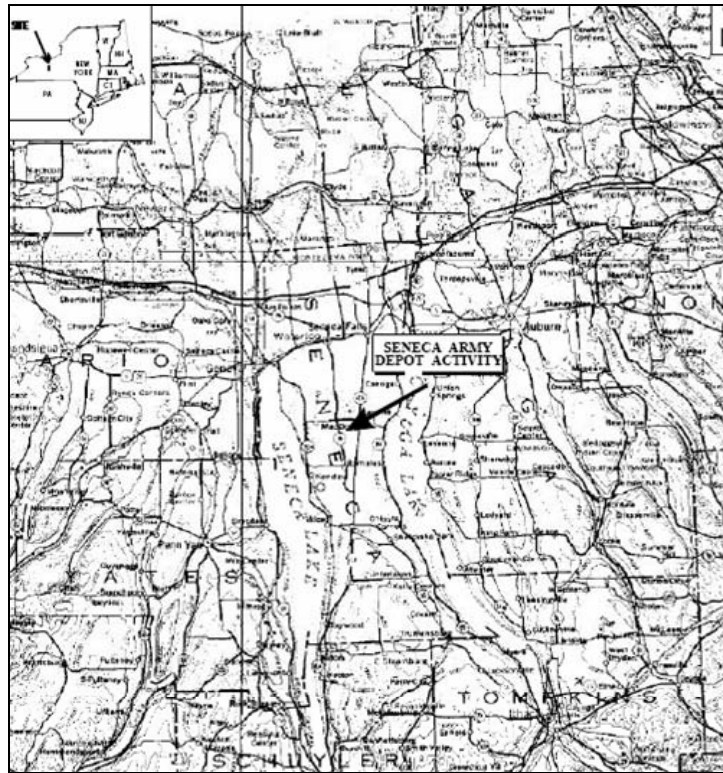
Figure 1. Location of Seneca Army Depot Activity. (Ref: Parsons Engineering, 2004)
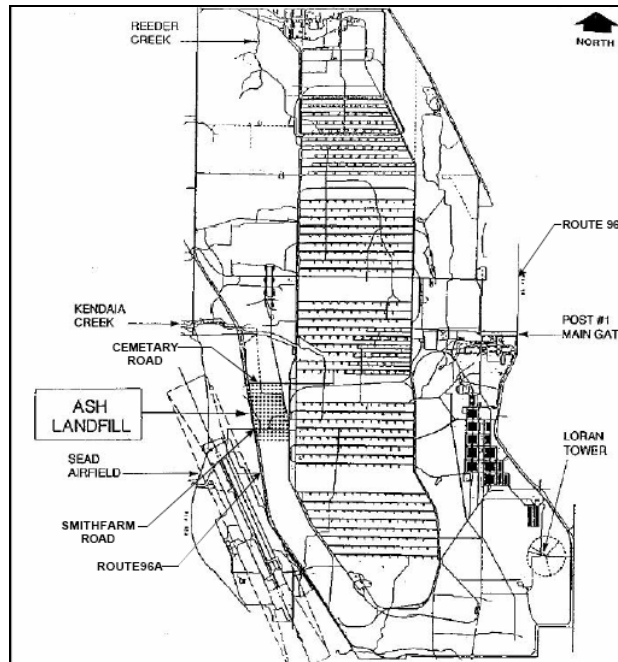
Figure 2. Location of Ash Landfill site. (Ref: Parsons Engineering, 2004)

Between 1979 and 1989, several Army agencies conducted groundwater and solid sampling at the Ash Landfill site to investigate the presence of Chlorinated Volatile Compounds (VOCs) in the local aquifer. These studies revealed the presence of an approximately 18-acres chlorinated plume, emanating from the northern western side of the landfill area, near the "bend in the road". Contamination due to PAHs and metals are also affecting the soil and groundwater of the area, but to a lesser extent. To remove the VOCs from the aquifer, several remedial alternatives have been implemented. Results have been mostly satisfactory. In addition, an extensive list of remedial options is provided in the report prepared by Parson in July 2004 (Final Record of Decision for Ash Landfill). These remedial options are compared based on many factors including: Overall protection of human health and environment, compliance with ARARs, Long term effectiveness and permanence, reduction in toxicity, mobility, or volume, short term effectiveness, implementability, and finally, costs. The aim of the remedial activities is to restore the aquifer underneath the Ash landfill site so that it can be transformed into a conservation/ recreation area.

1.2   Present Operation

As a result of Base Closure, SEDA has downsized significantly from 1200 to 140 employees. Following recommendation by DoD, approval by the Base Closure Commission, the President and Congress, SEDA was approved for the 1995 Base Realignment and Closure (BRAC) list in October 1995. The mission closure date was scheduled for September 30, 1999. Installation closure date was September 30, 2000, with 22 employees after that date. Current reuse plans project that most of the property will be transferred to the state for a wildlife refuge; some parts of the base will be transferred to various prison and correctional authorities.

A-3

1.3 Selection of Site

The Seneca site was selected to be modeled using the NAS tool due to two important characteristics. The first characteristic is the comprehensive field data set gathered in the area. For instance, information regarding the plume concentration has been constantly collected since 1990. This provides us with sufficient field data to test and validate the NAS tool. The redox condition existing in the aquifer can be determined by using the information collected since 1997. This data set is composed of oxygen, Fe(II), nitrate-nitrite, sulfate, and methane. In addition to redox and concentration information, the monitoring program conducted in this site also gathered information regarding the fluctuation of the water table with time. This information is fundamental to determine the influence of the flow direction on the concentration measured in the monitoring wells. This information is available from 1995 to 2003.

This site provides an opportunity to apply NAS to a source excavation and test the TOS option at multiple downgradient monitoring wells. Between 1994 and 1995, the contaminant source was partially removed, causing a reduction in concentration in the monitoring well located downgradient. The information collected before and after the removal action helps to validate and test the NAS capabilities to model source removal. In addition, the hydrogeology (glacial till) provides a unique setting for an application using NAS.

2.0 Site/Facility Characteristics

2.1 Hydrogeology

Two hydrogeological units are present in the Ash Landfill site. The superficial geological deposit is composed of glacial till. This layer is primary composed of clay, with sand and gravel also present in a lower percentage and with variable distribution. This variability in composition results in a broad range of hydraulic conductivities. Within the boundaries of the site, the thickness of this unit does not exceed 20 feet. The second hydrogeological unit is black fissile shale with small intebedded limestone layers. The first 5 feet of the shale are weathered as a result of erosive processes. Accordingly, the main aquifer of the zone is formed by the glacial till along with this weathered shale unit. The bedrock to this aquifer is the unaffected shale unit, which has an approximate thickness of 500 feet.

Water balance analyses conducted in this area have revealed that most of the groundwater recharge occurs in March and April. This causes the water table to reach its highest level during spring. During late summer, and specially, early fall, the water table drops dramatically to levels close to the bottom of the aquifer.

2.2 Source and Plume Description

After the landfill was closed in 1979, investigations were completed to study the potential disposal of contaminant to the soil and groundwater at the Ash Landfill site. The investigations showed that the aquifer was polluted with Volatile organic compounds (VOCs). Semivolatile organics and metals, such as copper, lead, mercury, and zinc, were also detected in the groundwater and soil at this site, but to a lesser extent. The longitudinal and transversal extension of the Chlorinated plume is 1,300 ft and 625 ft, respectively. The vertical migration of the plume is believed to be restricted to the upper till/weathered shale aquifer.

The data collected showed the presence of TCE in 33% of the groundwater samples. Similar number was registered for total 1,2-DCE. Conversely, VC was detected only in 7% of the samples. This contaminants break down clearly indicates that the redox conditions existing in the aquifer promote the reductive dechlorination as the preferential biodegradation process.

The monitoring program conducted in the Ash Landfill site revealed that the VOCs source was located within the Ash Land fill. More specifically, the collected concentration data indicates that the source is situated in the area nearby the monitoring well MW-44A. Following investigations, however, suggest that the VOC plume has it origins in more than one source. This remark arouse after treating the polluted soil near well MW-44A between 1994 and 1995. VOC groundwater concentration at well MW-44A dropped by more than 95 percent. However, other wells, such as PT-18 and MW-29, continued registering significant contaminant levels in the following years to the removal action. The existence of an alleged VOC source nearby Well PT-18A may account for this slender concentration reduction in these wells.

2.3 Past and Current Remediation Strategies

Three removal actions have been conducted since the VOCs plume was detected at the Ash Landfill. The first action consisted of the removal of an underground storage tank (UST) located nearby the incinerator building. This UST was used to store heating oil and it was an alleged source to the VOCs plume. Following studies, however, revealed that the tank was intact and no evidence of tank leakage was observed in the surrounding of the tank location. The UST was removed in April 1994.

The second action consisted of removing an alleged contaminant source. Sampling conducted in the Ash Landfill site revealed that the highest concentration of VOC was registered in the monitoring well MW-44. This suggested that the contaminant source was located somewhere nearby this well. Accordingly, between 1994 and 1995, a non-time critical removal was performed in this area; specifically in a sector known as "Bend in the Road". The remedial treatment consisted of removing approximately 35,000 tons of soil in this area and heating it to 800-900 F. The treated soil was then used to fill the excavated area. The surface treated area involves approximately 1.5 acres. The benefits

of this remedial action have been lately observed as the levels of VOCs in the groundwater have decreased by more than 95 percent in the treated area.

Finally, the last remedial action conducted in this area was the construction of a 650-foot long permeable reactive iron wall near the property line. This permeable wall was built in December 1998 with the purpose of controlling the migration of the plume by speeding up the reductive chlorination process in the groundwater . While quality data collected in the wall zone revealed that this permeable wall is quite efficient in removing chlorinated from the aqueous phase, the resulting aqueous concentration levels are still over the maximum level acceptable. A study concluded that better removal rate is to be expected when a longer reactive residence time is imposed.

Further prospective remedial alternatives are analyzed and compared in the "Final Record of Decision for Ash Landfill Seneca Army Depot Activity, Roulus, N.Y.", July 2004, prepared by Parsons. In that report, the remedial actions are analyzed in terms of Source Control and Migration Control. Source Control encompasses all the remedial alternatives that are intended to reduce the contaminant concentration at soil/sediment, such as, removal of sediments. Conversely, Migration Control incorporates the remedial alternatives that manage and control the migration of the plume. All the migration/source control alternatives are compared based on many factors including: Overall protection of human health and environment, compliance with ARARs, long term effectiveness and permanence, reduction in toxicity, mobility, or volume, short term effectiveness, implementability, and finally, costs. The selected remedy is composed of several elements that include excavation and off-site disposal of debris piles and installation of three permeable reactive barrier walls. It also considers a contingency plan in the event that the acceptable groundwater concentrations downgradient the site are exceeded.

2.4   Groundwater Flow and Transport Modeling – Previous work

The transport of contaminant was evaluated using an analytical transport model called ODAST. This model is based on the analytical one-dimensional groundwater transport model presented by Van Genutchten and Alves (1982). Its application on the SENECA site assumes that the contaminant is migrating along an infinite, homogeneous, and isotropic porous media. Furthermore, the flow field is assumed to have reached steady state. The contaminant source was considered to be sufficient large so that it remains constant over time. This assumption is valid as the model was built before the performance of the non-time critical removal in the Landfill area. The SENECA aquifer presents primarily two plumes: TCE and 1,2-DCE. To predict the migration of them, ODAST was used to model each contaminant independently. The calibration and sensitivity analysis conducted to determine the best parameter set value yielded a seepage velocity of 18.1 ft/yr and values for the decay constant of 0.000622 day^{-1} (TCE) and 0.000699 day^{-1} (DCE).

3.0 Demonstration Approach

3.1 Modeling Objective

This site provides an opportunity to apply NAS to a source excavation and test the TOS option at multiple downgradient monitoring wells. Because source removal was not complete and contaminant source concentration in groundwater only decreased by about 50%, the observed post-remediation source concentration was used to estimate the decrease in concentration at downgradient monitoring wells.

3.2 Input Parameters

3.2.1 Hydrogeologic Data

The monitoring program conducted at the Seneca site permits a fairly reasonable characterization of the plume. The extension of the contamination is clearly defined, but the concentration distribution inside the plume cannot be readily established. Furthermore, the location and the dimension of the contaminant source cannot be determined from the field data. In this section, the available field data is analyzed and filtered. Later, the filtered information is used by NAS to determine the best hydrogeological parameter values range capable of reproducing the fate of the contaminant. Input parameters used in NAS simulations are shown in Table 1.

Table 1. Hydrologic parameters used in NAS simulations

Site Information	Parameter	Unit	Minimum	Average	Maximum
Hydrogeologic	Hydraulic Conductivity	ft/year	479	599	718
	Hydraulic Gradient	ft/ft	0.02	0.03	0.04
	Weight Percent Organic Carbon	(%)			0.08
	Total Porosity	ft^3/ft^3		0.3	
	Effective porosity	ft^3/ft^3		0.2	
	Transport Velocity	ft/year	47.9	89.85	143.6
Source	Length	ft		100	
	Width	ft		30	
	Contaminated aquifer thickness	ft		5	

3.2.2 Source Characteristics

Between August 1994 and June 1995 a partial source removal was conducted at the Ash Landfill located in the Seneca site. The remedial action consisted of excavation and thermal treatment of VOCs impacted soils. After the soil was treated, it was backfilled into the excavation area. Source zone monitoring well data show that complete remediation was not achieved and that hot spots of contamination remained. Specifically,

TCE concentration declined from 12,000 to 5300 μg/L, and as a consequence of this partial source removal, the concentration levels at the downgradient wells showed a declining trend. Analysis of the hydraulic gradient flow direction indicated considerable variability over time resulting in fluctuation in VOC concentration values of time. Because of the observed time fluctuation in concentrations, average trends in the pre- and post-source removal data were employed for NAS simulations.

3.2.3   NAC Analysis – Plume centerline concentrations and redox zonation

Figure 3 shows the stable pre-remediation TCE plume and the best-fit analytical solution using data collected immediately prior to the completion of the source excavation. Due to the lack of DCE concentration data before the partial source treatment period, the NAS application was based entirely on the TCE data. A single redox zone best represented the conditions in the ground-water system. The redox conditions existing in the aquifer were determined by using the information collected since 1997. This data set is composed of oxygen, Fe(II), nitrate-nitrite, sulfate, and methane. The aquifer is primarily anaerobic in nature, but high concentrations of sulfate (> 200 mg/L) may mask the exact redox condition. Low levels of Fe(II) and methane and consumption of sulfate along the ground-water flow path suggest that sulfate-reducing conditions are present in the plume. Contaminant data clearly supports that the redox conditions existing in the aquifer promote the reductive dechlorination as the preferential biodegradation process.
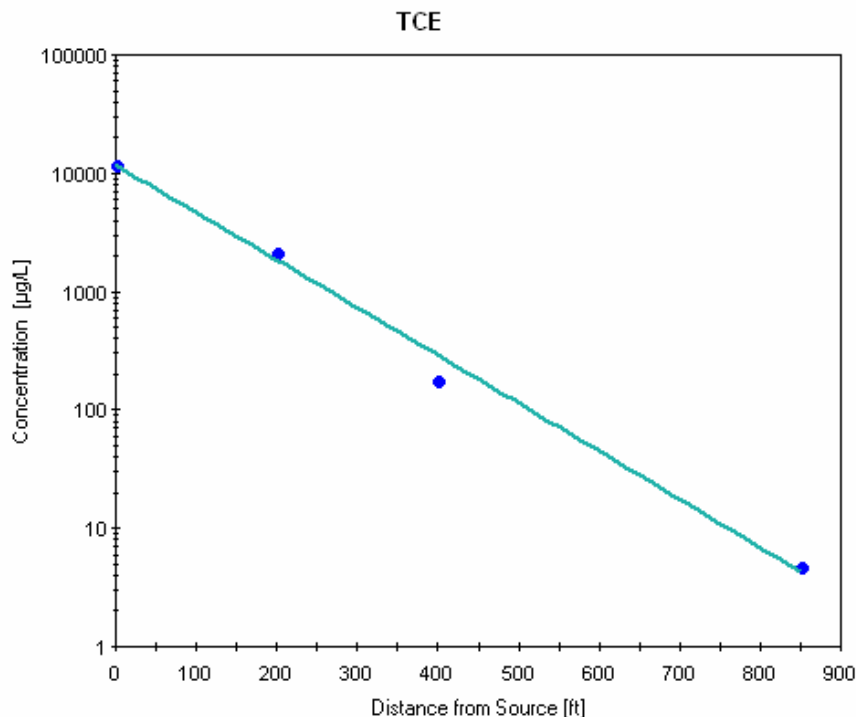
Figure 3. Observed and NAS-simulated TCE concentration versus distance along plume centerline prior to source concentration reduction.

4.0   Performance Assessment

The concentration field data collected at the Seneca site is strongly influenced by the flow direction. For this reason, the assessment of the model outputs quality is carried out by comparing the model results against the average observed data. Given that two different data trends are identified during the monitoring program (before and after the removal action), the comparison must be conducted for both periods separately. Table 2 summarizes the NAS predicted concentration pre/post source removal along with the mean field data for each period. The table also provides the root mean of squared residual error (RMS) for the entirely period.

Table 2. Observed Time-Averaged Concentration Data

Monitoring Well	Average Field Data Before Removal	Average Field Data After Removal	Average NAS Simulation Before Removal	Average NAS Simulation After Removal	RMS
PT-18A (Source)	11776	5307	11776	5903	4949
PT-12A	2165	1327	2184	1203	673
PT-22 (21A)	619	378	681	341	110
MW-29	5	-	2.2	-	3

Breakthrough curves at wells PT12A and PT22 (distances of 180 and 400 ft downgradient of the source, respectively) and shown in Figure 4, respectively. A match between the predicted and observed curve is, to some extent, possible only at well PT-12A. Data gaps in the mid-1990s and along with the time fluctuation in concentrations, hinders the accurate estimation of the observed breakthrough time. The breakthrough and inflection points are difficult to judge from the data but in general, a reasonable fit was obtained at both wells. Changes to the source concentration reduction provided an improved fit to the final observed concentration at Well PT21A but resulted in a poorer fit to the data at Well PT12A. The data trend at Well MW-29 was insufficient for the TOS analysis. Concentration data may have been impacted by the installation of a permeable reactive barrier in the vicinity of Well MW-29.

5.0   References

Parsons Engineering. 2004. Final Record of Decision for Ash Landfill at Seneca Army Depot Activity, Romulus, NY (Contract Number: DACA87-95-D-0031).
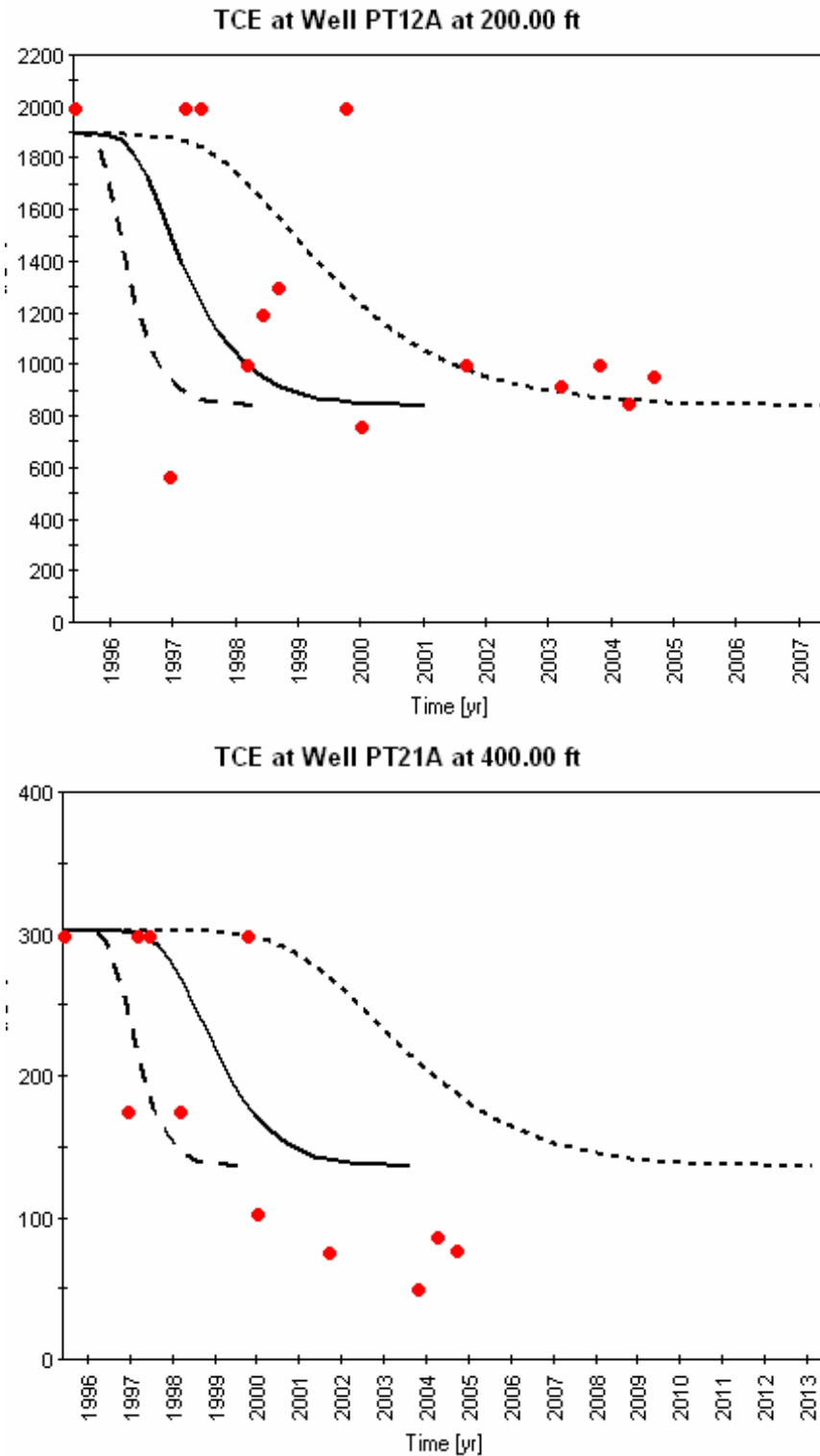
Figure 4. Observed and NAS-simulated TCE concentration versus time at downgradient wells based on the observed source concentration reduction.

Appendix B: Niagara Falls, NY – USGS (Textron) Site

Niagara Falls, NY – USGS (Textron) Site

1.0   Test Site

1.1   History of Operations at the Site

The Textron Realty Operations Incorporated Facility is located at 2221 Niagara Falls Boulevard, Wheatfield, New York. The plant is approximately 2 miles north of the Niagara River, and 5 miles east of Niagara Falls. Activities at this aerospace-defense company facility included the development and manufacturing of navigational and guidance systems. The facility has a neutralization pond (NP), a rectangular basin measuring 60 ft by 100 ft by 10 ft, which, from approximately 1940 to 1987, was used to collect wash water from rocket engine test firings, and received storm runoff, cooling water, and coal gasification wastes. The NP was closed in 1988, and by 1990, a plume of TCE and its metabolites extended approximately 5000 ft south of the facility. A smaller plume of dense non-aqueous-phase liquids (DNAPL) probably serves as a continuing source of TCE. The NP is a Resource Conservation and Recovery Act (RCRA)-regulated unit, subject to both RCRA post-closure requirements and corrective action. The NP is currently regulated as a hazardous waste disposal unit under a New York State Part 373 post-closure permit which was initially issued in 1992 and renewed in 1998. Module III (Corrective Action) of this permit was amended in 2002. The current permit expired in 2003 but is still in force until permit renewal in 2005 (USEPA 2004, Yager 2002).

1.2   Present Operation

The facility is no longer in use as a manufacturing plant. Remediation at the site is on-going.

1.3   Selection of Site

The primary attributes of this include a fractured rock aquifer with a DNAPL source that well-documented in previously published work by the USGS (Yager 2002). Secondly, the ground-water extraction system allows testing of the NAS pump-and-treat option.

2.0   Site/Facility Characteristics

2.1   Hydrogeology

The facility overlies 16 to 40 ft of unconsolidated deposits underlain by the upper part of the Lockport Group, a 170 ft thick petroliferous dolomite. Zone 1, the uppermost part of the Lockport Group which corresponds to the Guelph Formation, is 10 to 20 ft thick and comprises the weathered bedrock layer that contains many open fractures, some of which have been widened by dissolution. Zone 1 also contains a water-bearing, horizontal-fracture zone near its lower contact with Zone 2, the next lower part of the Lockport Group which corresponds to the upper part of the Eramosa Formation. Zone 2 is an 8 ft

thick bituminous dolomite that appears relatively unfractured, but the presence of chlorinated ethenes in a limited area within the underlying Zone 3 indicates that some high-angle fractures probably penetrate Zone 2 and form pathways for downward migration from Zone 1. The TCE remains primarily within Zone 1, which will remain the focus of this assessment.
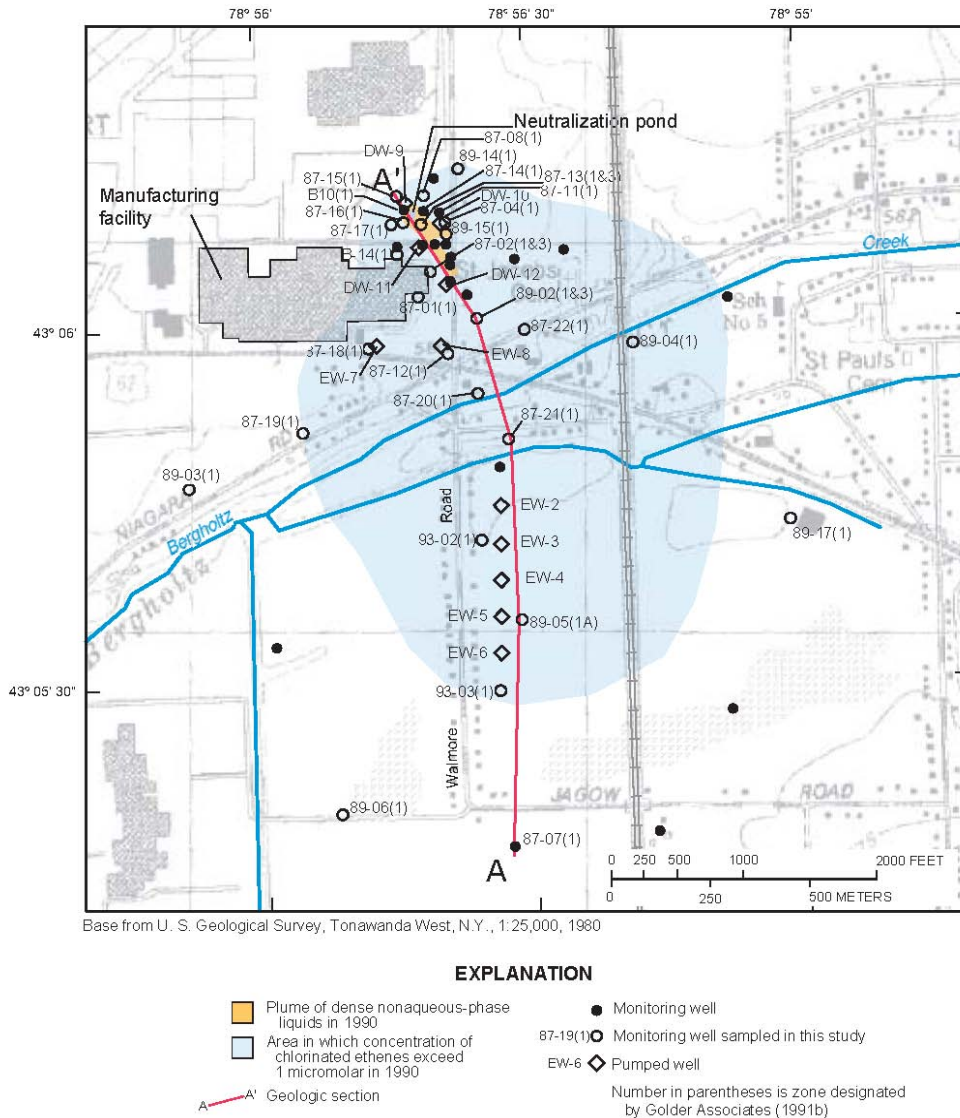
Figure 1. Site Map. (Ref: Yager, R.M., 2002)

The primary water-bearing zones in the Lockport Group are the weathered bedrock surface and horizontal-fracture zones which are connected by high-angle fractures and by subcrop areas where the fracture zones intersect the bedrock surface (Figure 2). Groundwater flows southward and westward through the Lockport Group, under the natural hydraulic gradient, from recharge areas near the Niagara Escarpment north of the facility, toward discharge areas in low-lying areas near the Niagara River to the south. Cross-hole pumping tests showed a Zone 1 transmissivity estimate of about 65 ft^2/d, a hydraulic connection throughout Zone 1, and no vertical connection apparent between Zones 1 and 3. Groundwater velocity was computed to range from 0.7 to 3 ft/d, from an

assumed effective porosity of 3%. To limit the migration of the aqueous phase contaminants, a system of five offsite recovery wells began pumping groundwater from Zone 1 in 1993 at a combined rate of 9360 ft^3/d. The gradient induced by pumping has altered the natural direction of groundwater flow south of the facility and induced an upward vertical gradient from Zone 3 to Zone 1. Water in Zone 1 has dissolved solids concentrations of 1,000 to 5,000 mg/L, predominantly calcium and sulfate. Dissolved oxygen concentrations were less than 0.4 mg/L. Hydrogen concentrations ranged from 0.2 to 0.6 nM, which indicated iron-reducing conditions. This conclusion is supported by the presence of ferrous iron (Fe^{2+}) at concentrations above 0.02 mg/L in many wells. Ferrous iron concentrations are generally greater than 0.1 mg/L where sulfide concentrations are less than 1 mg/L, but sulfide is present in concentrations as high as 18 mg/L in Zone 1. The presence of sulfide would maintain anaerobic conditions by removing any available oxygen through the oxidation of sulfide to sulfate, and also lower the concentrations of ferrous iron through the precipitation of iron sulfide. Some of the methane could be derived from a natural gas reservoir that is present locally in the Lockport Group and in underlying rocks (Yager 1997, Yager 2002).
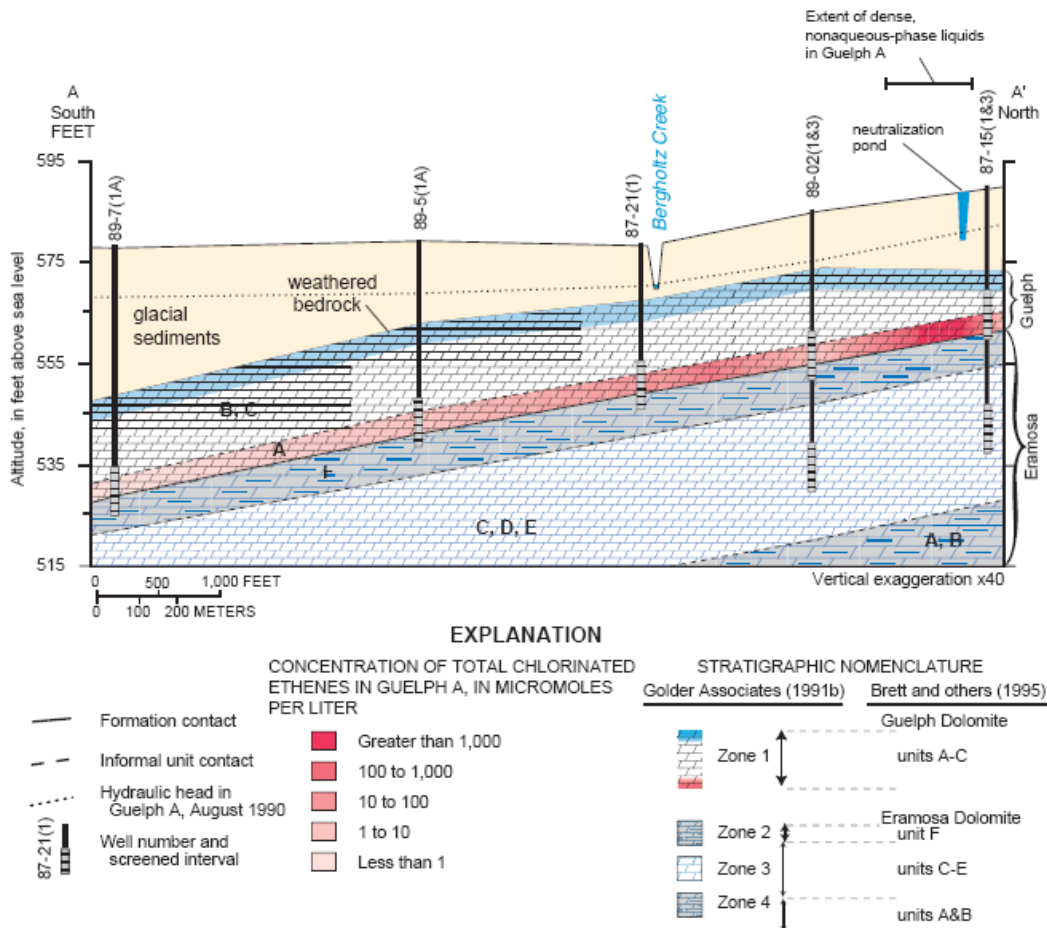
Figure 2. Vertical section A-A' through the chlorinated ethene plume (Ref: Yager 2002).

2.2   Source and Plume Description

The RCRA Facility Investigation (RFI) concluded that hazardous waste constituents from the NP have been released to the soil and groundwater beneath the facility. The hazardous waste constituents, primarily volatile organic compounds (VOCs) are present in the groundwater as aqueous phase contaminant plumes and as a plume of DNAPL. Aqueous phase contamination has been found in the soils, in the unconsolidated sediments above the bedrock and in the bedrock. The extent of the DNAPL plume in the overburden appears to be limited to the facility property. The extent of the aqueous phase bedrock plume is considerably greater. Contamination in Zone 1 extends as a pear-shaped plume from the NP to approximately 5000 ft southeast of the NP. The plume travels in the upper bedrock aquifer, beneath residential and commercial areas, posing a potential for volatile vapors to migrate from the plume into buildings. On-site, the facility conducted VOCs analysis of air samples in 2000. The readings were significantly below the limits allowed by the federal Occupational Safety and Health Administration. The NP was dewatered in 1984, then sludge and soils were removed in 1987, and the unit was closed in 1988 by placement of a low permeability clay cap. All contaminated soil found in the NP was removed and sent off-site to a permitted landfill. (USEPA 2004)

2.3   Past and Current Remediation Strategies

The facility wrote a corrective measures study (CMS), which was approved in 1991. The CMS included a baseline risk assessment, which concluded that the greatest risk of exposure was from the Zone 1 groundwater downgradient from the facility, if extracted for domestic purposes. Zone 1 is the most contaminated portion of the site; however, the contaminated groundwater is not used as a source for the surrounding community's drinking water. Therefore, the objective of corrective measures is to mitigate the dissolved phase plume in Zone 1. However, to effectively mitigate the dissolved phase plume, the source of the plume (the DNAPL plume) would need to be removed or contained. Due to the physical characteristics of the DNAPL, remediation by pumping or other extraction methods is not technically feasible. The effective alternative is to control the dissolution of the DNAPL by hydraulically or physically containing it. By hydraulically containing the DNAPL, risks of further off-site migration of the source of the dissolved phase contamination can be eliminated. To address the existing contamination and remediate the areas impacted by the contamination, the facility has installed an off-site and an on-site groundwater extraction system. The operation of the off-site and on-site groundwater extraction systems started in 1993 and 1995 respectively. The off-site system currently consists of four extraction wells. Each extraction well is connected by an underground pipeline that discharges extracted groundwater to a sanitary sewer inlet for treatment at the Niagara County Sewer District treatment plant. The off-site system is currently achieving its design goal of maintaining a groundwater capture zone that extends to the limits of the dissolved phase plume. The on-site system consists of six groundwater extraction wells. It is also meeting its design objectives, which are to control off-site migration of contaminated groundwater and eventually attain the New York State groundwater standards. Each on-site extraction well is connected to an underground pipeline that discharges to an on-site treatment plant. The results indicate

that, in general, contaminant concentrations detected in groundwater samples from both the on-site and off-site Zone 1 monitoring wells are gradually declining, as anticipated. A reduction in contaminant concentration has been noted in samples from the on-site overburden wells. Also, as indicated before, there are no on-site or off-site indoor air impacts. (USEPA 2004)

2.4   Groundwater Flow and Transport Modeling – Previous work

The presence of the TCE metabolites cis-1,2-dichloroethene (DCE), vinyl chloride (VC), and ethene in the plume, and the results of previous laboratory microcosm studies, indicate that the TCE is being degraded by naturally occurring microorganisms. Biodegradation rates of TCE and its metabolites were estimated through simulation with BIOMOC, a solute transport model that represents multispecies reactions through Monod kinetics. A fracture layer in Zone 1 was represented as a porous medium containing an extensive, 3-foot thick layer with interconnected fractures; this layer is bounded above and below by subhorizontal stratigraphic contacts. The Monod reaction constants were estimated through nonlinear regression to minimize the difference between computed concentrations of TCE and its metabolites, and the concentrations measured before and during 5 years of pump-and-treat remediation. Transport simulations indicated that, by April 1998, the chlorinated ethene plume had reached a dynamic equilibrium between the rate of TCE dissolution and the rate of removal through pumping and biodegradation. Biodegradation of chlorinated ethenes at the site can be simulated as first-order reactions because the concentrations are generally less than the half-saturation constants estimated for Monod kinetics. Computed degradation rates are proportional to the estimated ground-water velocity, which could vary by more than an order magnitude at the site, as indicated by the estimated range of fracture porosity (3 to 0.3 %). Chlorinated ethene concentrations of April 1998 were better reproduced when the TCE source was represented as a constant concentration than as a constant flux, because the latter predicted that the plume would dissipate after 5 years of pump-and-treat remediation. This result indicates that the rate of TCE dissolution is not limited by the mass of TCE in the DNAPL plume. Simulation of diffusion by the transport model MOC3D indicated that concentrations of these contaminants within the rock matrix surrounding the fracture zone were relatively unchanged after 5 years of pump-and-treat remediation. The principal sources of uncertainty in the prediction of biodegradation rates and of the fate of chlorinated ethenes at the site are the fracture porosity and DNAPL mass in the aquifer. (Yager 2002)

3.0   Demonstration Approach

3.1   Modeling Objective

The NAS modeling objective was to hold the previously mentioned parameters constant, and vary three additional parameters to find the best correlation between NAS-estimated TCE concentration-versus-time curves and observed data.

3.2 Input Parameters

3.2.1 Hydrogeologic Data

Hydrogeologic and source zone parameters used as constant values for all NAS simulations were obtained from previous engineering studies and modeling reports (Table 1). Hydraulic conductivity, hydraulic gradient, and effective porosity (5.56 ft/d, 0.0076 ft/ft, and 3 % respectively) were input to NAS from the 2004 annual groundwater extraction system performance report (Shaw 2005). From this input, NAS estimated a groundwater velocity of 1.44 ft/d, as also reported in the document (Shaw 2005). A weight percent organic carbon value of 0.01 % was input to NAS such that the retardation factor for TCE would equal 2.5 as per the previous USGS modeling investigation (Yager 2002). The contaminated aquifer thickness is input as 3.5 ft (Yager 2002). For all NAS simulations, the current contaminant dataset was 04/01/1993, and the initial concentration source well was set to the second well, Well 87-20(1), thereby setting the initial TCE concentration before pumping to approximately 26 mg/L (Yager 2002). The TCE decay rate initially ranged from a minimum of 0.0006 1/d (Yager 2002) to a maximum of 0.0065 1/d (from averaged decay rate values of all NAS datasets: which represents the highest rate including the contribution from the pumping well).

Table 1. Hydrologic parameters used in NAS simulations

Hydrogeology	Report
Hydraulic conductivity	5.67 ft/d
Hydraulic gradient	0.0076 ft/ft
Weight percent organic carbon	0.01 %
Total Porosity	3 %
Effective Porosity	3 %

3.2.2 Source Characteristics

NAPL mass ranged from 100 to 10,000 kg within a well-defined source zone (Table 2). The pump-and-treat average saturated thickness ranged from 3.5 to 10 ft (approximated from Yager 2002; this, in effect, varied the NAS-estimated, effective pumping rate from the actual contaminated aquifer thickness – 3.5 ft). NAS source length and source width are both specified as 933 ft such that the DNAPL plume source area approximates 20 acres as per Yager (2002. The Pumping Rate, distributed along the average saturated thickness, for Well EW-2 was specified as 1540 ft^3/d (8 gpm – Shaw 2005).

4.0   Performance Assessment

Simulation of C vs time – Sensitivity to mass estimate
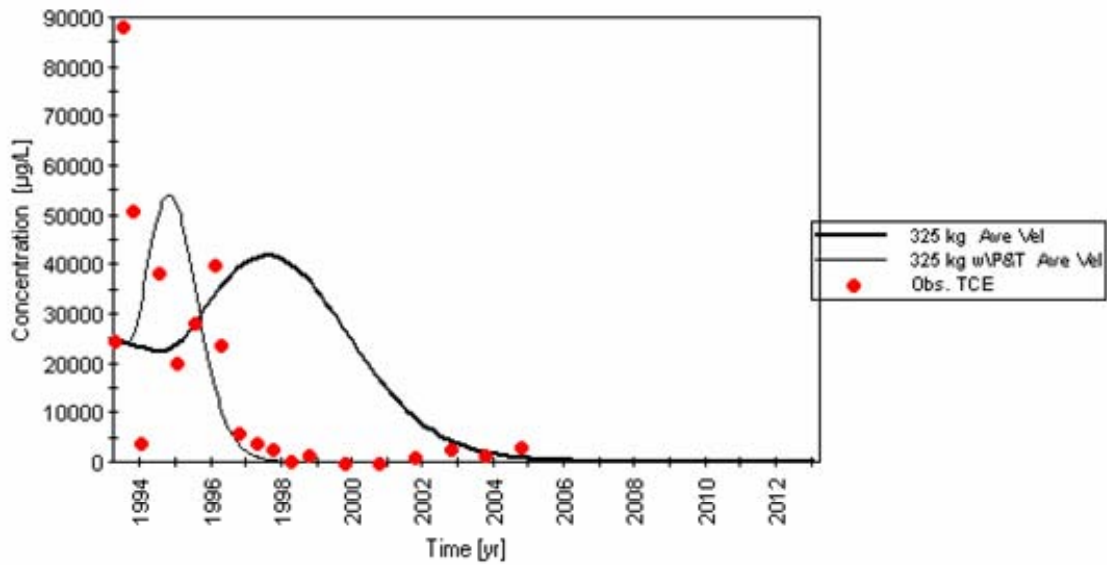
Figure 3: NAS-estimated vs. Observed TCE - Decay Rate =0.0006 1/d, Average Saturated Thickness=3.5 ft, NAPL Mass =325 kg.
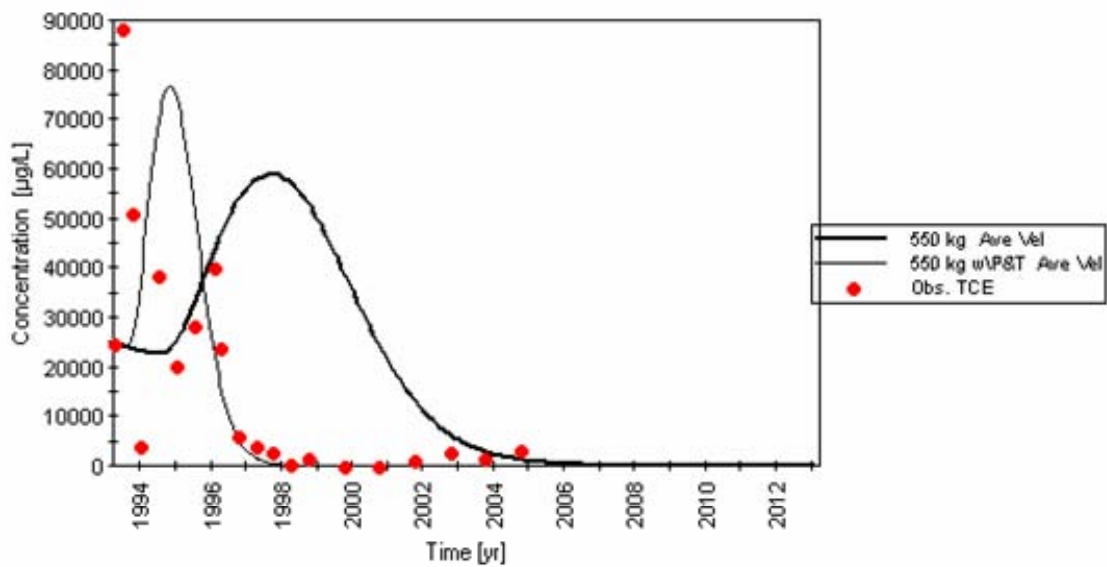
Figure 4: NAS-estimated vs. Observed TCE - Decay Rate =0.0006 1/d, Average Saturated Thickness =3.5 ft, NAPL Mass =550 kg.

Simulation of C vs time – Sensitivity to mass estimate
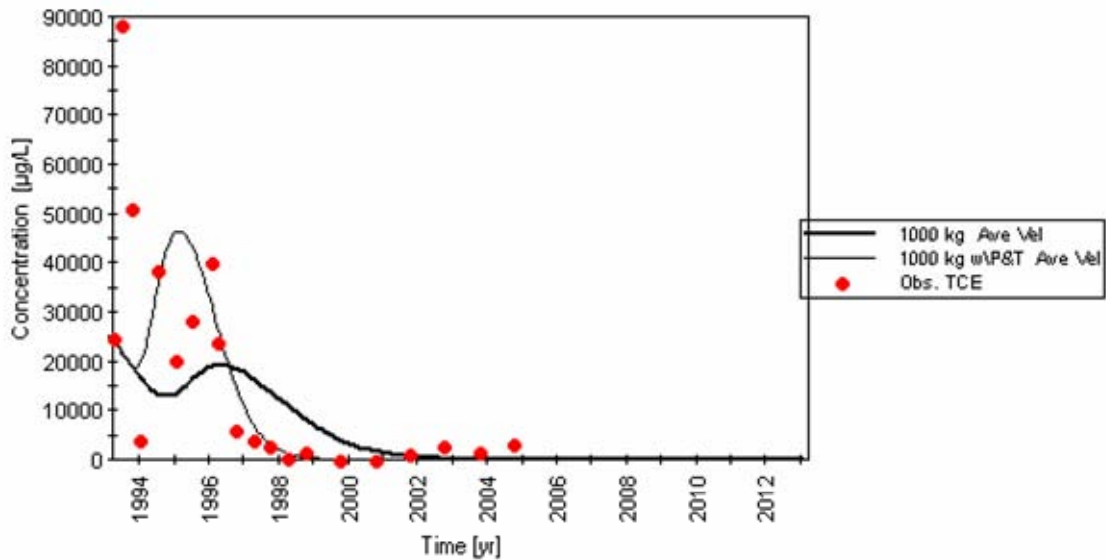
Figure 5: NAS-estimated vs. Observed TCE – Decay Rate=0.0035 1/d, Average Saturated Thickness =6.75 ft, NAPL Mass =1000 kg.
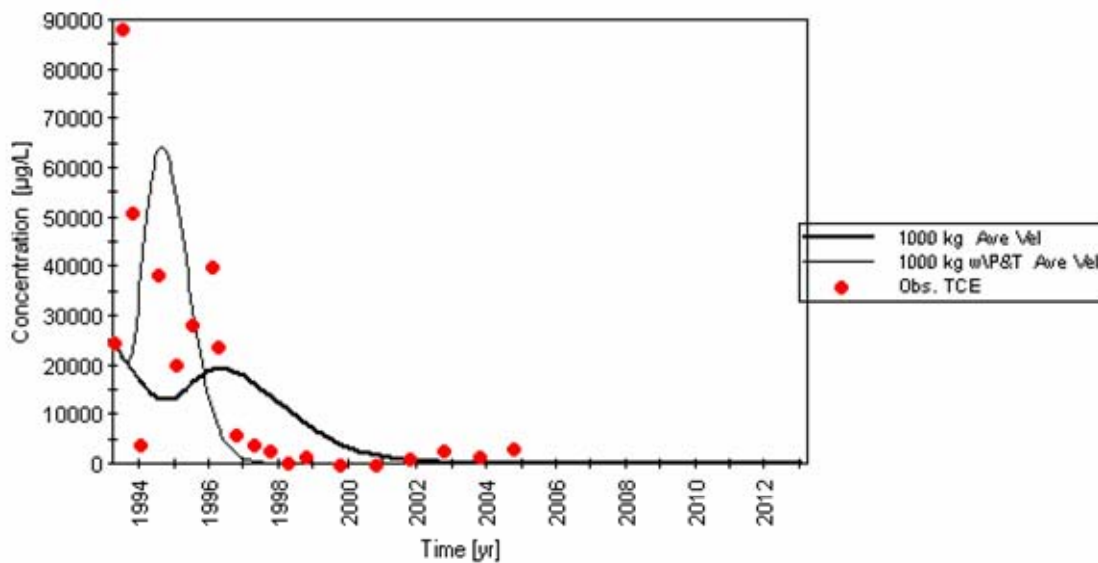
Figure 6: NAS-estimated vs. Observed TCE - Decay Rate =0.0035 1/d, Average Saturated Thickness =3.5 ft, NAPL Mass =1000 kg.

The values for TCE decay rate and average saturated thickness fall within acceptable ranges (Yager 2002). The previous study transport models (Yager 2002) were calibrated to the total estimated mass of TCE (1090 kg) removed by pumping from March 1993 to April 1998. This number is well within the range estimated by NAS for NAPL mass. Therefore, NAS-estimated values are shown to correlate well with both observed data

and as well as with estimates from previous modeling efforts. These results are significant in showing that NAS was successful in a novel application to a fractured-bedrock site, and may well be successful in analysis of other fractured-bedrock sites.

5.0 References

U.S. Environmental Protection Agency, 2004, Textron Realty Operations, Inc. Fact Sheet.

Yager, R.M., 2002, Simulated Transport and Biodegradation of Chlorinated Ethenes in a Fractured Dolomite Aquifer Near Niagara Falls, New York: U.S. Geological Survey Water-Resources Investigations Report 00-4275, 55 p.

Yager, R. M., S. E. Bilotta, C. L. Mann, and E. L. Madsen. 1997. Metabolic adaptation and In situ attenuation of chlorinated ethenes by naturally-occurring microorganisms in a fractured dolomite aquifer near Niagara Falls, NY. Environ. Sci. Technol. 31:3138-3147.

Shaw Environmental and Infrastructure Engineering of New York, P.C., 2005, 2004 Annual Summary and System Performance Off-Site and On-Site Groundwater Extraction Systems Report.

Appendix C: NAES Lakehurst, NJ – Sites I & J

NAES Lakehurst, NJ – Sites I & J

1.0   Test Site

1.1   History of Operations at the Site

The Naval Air Engineering Station (NAES) Lakehurst station presents a surface of 7,412 acres and it is located within the Pinelands National Reserve in central New Jersey (Figure 1). In 1960s and subsequent years, disposal of industrial waste water into the groundwater and the use of solvent to degrease metal surfaces and dry cleaning establishments were usual on-site operations within the borders of this Naval Site. The consequences of these actions appeared in the late 1980's when analyses of groundwater quality conducted in this area revealed that these on-site operations caused the contamination of the aquifer. In particular for Areas I and J, the quality analyses indicated the presence of volatile organic compounds in the groundwater.
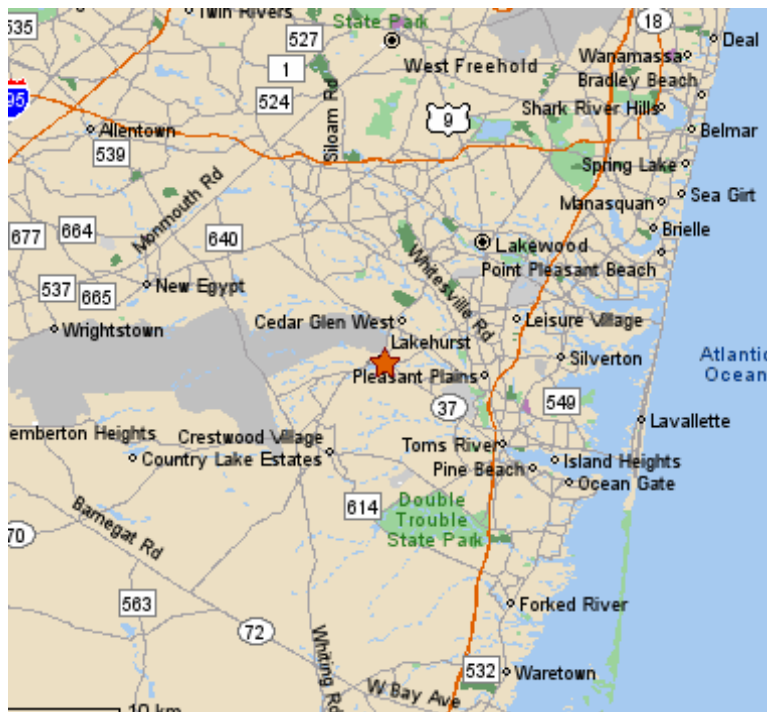
Figure 1. Site Location of Naval Air Engineering Station, Lakehurst, New Jersey. (Ref: www.lakehurstnj.org).

1.2   Present Operation

Currently, Lakehurst facility operates as the Aircraft Platform Interface Group for technical mission support. NAES is responsible for the catapults that launch the aircraft; the landing aids that guide them back to the ship; the arresting gear that recovers them on the deck; and all of the support equipment to move, service, and maintain aircraft. The base employs 1,898 civilians, 251 contractors, and 218 military personnel

1.3 Selection of Site

The selection criteria are mainly based on two characteristics; appropriate hydrogeological condition, and high-quality data sets. For the purpose of this study, appropriated hydrogeological condition is understood as a lithological configuration that embraces the flow through porous media rather than a conduit flow. It also permits the existence of a groundwater velocity faster than 5 feet/year. The second selection criterion is the existence of high-quality temporal and spatial data set. This data set must be available for redox parameters, contaminant concentrations, and hydraulic head distribution.

The aquifer underneath the Lakehurst site is sufficiently permeable to comply with the hydrogeological requirements. As for the quality data set, the monitoring program conducted in this site since 1996 has provided sufficient geochemical and contaminant chemistry data to understand the processes affecting the migration of the plume. These characteristics transform Lakehurst in an appealing site to test the NAS software.

2.0 Site/Facility Characteristics

2.1 Hydrogeology

In terms of regional geological setting, the NAES is located in the Atlantic Coastal Plane. This geological structure was formed as a result of depositional and erosional events occurred over the last 170 to 200 million years. The bedrock is composed of methamorphic gnesis and schist, and the sediments are mostly sands, clays, gravels, and marls. The oldest sediments of the coastal plain were deposited more than 100 million years ago. Subsequent to the initial deposition, multiple sea level transgressions and regression formed the existing sedimentary sequence. These geological events caused The Cohansey Sand Formation to be exposed throughout most of the county surface. This formation is permeable and constitutes one of the principal aquifers in the Ocean County. In the vicinity of the NAES, this formation has reported as being a characteristically yellowish-brown, unfossiliferous, cross-stratified, pebbly, ilmenitic fine to very coarse-grained quartz sand that is locally cemented with iron oxide. Based on excavations conducted within the NAES borders, the upper 20 to 100 feet of strata underlying the center is primarily a fine to coarse grained quartz sand. Fine gravel and silt is commonly present intermixed with the sand. The depth of bedrock in the surrounding area of the NAES Site is approximately 1,800 feet. Pumping tests conducted in the main aquifer of Area I yielded values for the horizontal hydraulic conductivity between 63 and 99 ft/day. The estimated specific yield ranged from 0.057 to 0.23.

The water table is typically shallow with regional values fluctuating between 6 and 40 feet below the surface. In the area underneath the NAES facilities, the water table reaches its highest level. For instance, the average depth of the water table at Site 3 (Area J), Site 6 (Area I), and Site 25 (Area I) are 7, 11, and 7 feet respectively.

The regional horizontal flow rate has been reported to be four feet per day. However, Dames and Moore (1999) report that the flow rate at the site is smaller and is equal to fifty five feet per year.

2.2   Source and Plume Description

The contamination in Areas I & J at Lakehurst Air Naval Station are primarily due to the discharge of water containing trichloroethene (TCE), hydraulic fluid and ethylene glycol, along with the steam-cleaning operation of various equipments.

The monitoring program revealed the existence of three VOC plumes; one North plume and two South plumes. In all three plumes is observed that the highest levels of contaminant are registered in deep wells (between 50 and 70 feet depth). The North plume starts in a region close to Site 25, and then, contaminants are transported by the groundwater system in the east direction approximately 5.000 feet. This plume is widely spread due to changes observed in the flow direction. The South plume nearest North plume (SP1) seems to have its source in the area covered by Sites 6, 7, and 24. The contaminant released in this area has been transported 4.000 feet in the east direction. The second South plume (SP2) moves from an area close to Site 3 towards the south-east a distance of 3.000 feet. The predominant constituent in these three plumes is DCE. The concentration data along with the redox information suggest that the plumes are in steady state and that an intrinsic biodegradation process is taking place. The locations of these plumes are included in Figure 2.
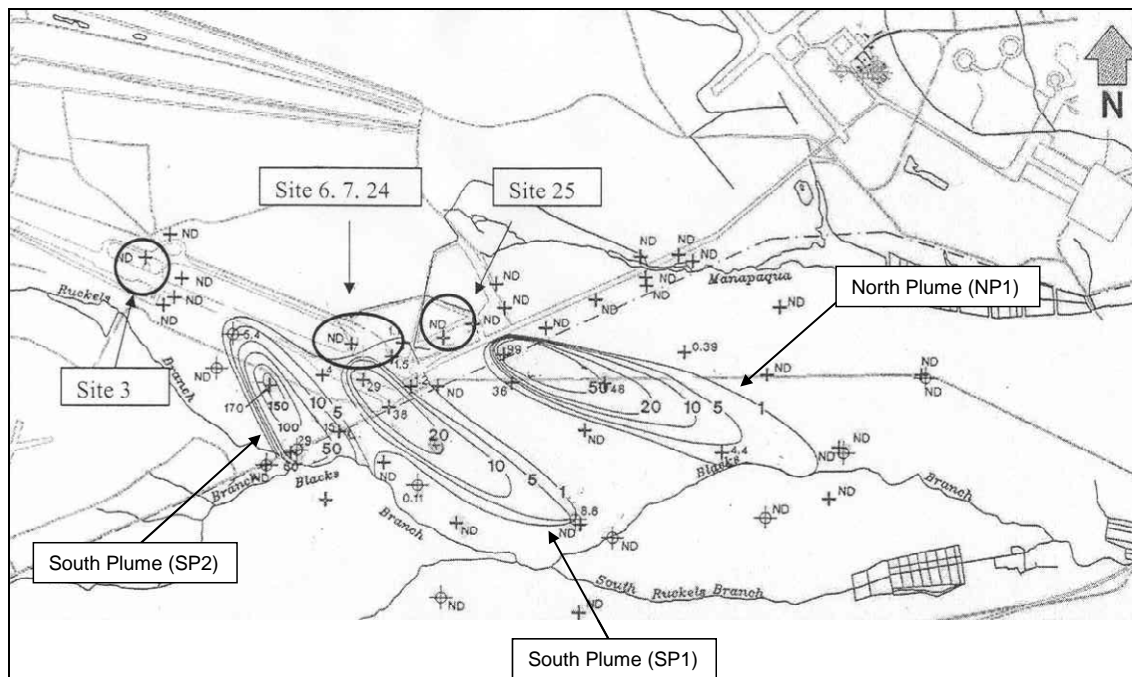
Figure 2. Location of plumes and potential sources. (Ref: Dames and Moore, 1999)

The groundwater sampling results and the on-site operations history indicate the presence of several area sources. However, this information is not sufficient to precisely determine the location, mass or geometry of each one of them.

2.3   Past and Current Remediation Strategies

The first remedial alternative proposed to clean the aquifer was a groundwater recovery, treatment, and recharge system. Later, a study conducted in late 1993 and early 1994 revealed that this system was not going to be effective in removing the contaminant. Furthermore, it will cause the loss of several acres of wetland. Instead, the natural attenuation approach was proposed as a new remedial alternative to restore the aquifer. The monitoring natural attenuation remedial alternative started in 1996 and it has proved to be efficient in degrading the Volatile Organic compound plume in Areas I and J. The data collected during this monitoring program has shown that existing geochemical and biological conditions at site are stable. Thus, the biodegradation processes observed to date can be expected to continue in the future.

2.4   Groundwater Flow and Transport Modeling – Previous work

In 1997, Beatty Franz & Associates Limited developed the first groundwater flow and contaminant transport model for Areas I & J (1997 Annual Report Groundwater Restoration Study Areas I and J - Brown & Root, 1997). The groundwater flow model and the transport model were built using the Visual MODFLOW and the MTD3 packages, respectively. Results from the flow model indicated that the observed hydraulic head distribution could be reasonably predicted by using different combinations of hydraulic conductivities and recharges values. To reduce the uncertainties around these parameters, the study proposed gathering more detailed information regarding hydraulic conductivities and recharges from creeks. In regards to the transport model, its prediction matched the total chlorinated concentration distribution observed in the field. However, the concentration distribution for each constituent could not be determined due to limitations associated to the MT3D transport model code. According to the study, this limitation is overcome by building the transport model using the RT3D package instead. In addition to provide concentration distribution for all contaminant, this package allows the incorporation of biodegradation processes in the simulation.

In 1999, Dames & Moore Inc. was contracted to update the flow model and to build a new transport model. This task was conducted following the findings and recommendations drawn from the 1997 Annual Report Groundwater Restoration Study Areas I and J (Brown & Root, 1997). The updated flow model has 4 layers, with 229x138 cells per layer, and a grid spacing of 80 ft by 80 ft. An alternative one-layer flow model was also built with similar features to the four-layer model. Because of both models provide similar results when coupled with the transport model, the simulations employed the one-layer model. The transport model assumes that the contaminant was released into a clean groundwater system in 1958. The sources are modeled as constant boundary conditions, depleting in the year 1990 (South Sources) and in the year 2017 (North Sources). The resulting transport model provides concentration distributions that

reasonably compare to the observed plumes. The calibrated model was used to predict the migration of the plume for the year 2002, 2012, 2017, 2022, 2032, and 2042. Results indicate that all contaminant concentrations are to be below 1 ppb by the year 2042.

3.0   Demonstration Approach

3.1   Modeling Objective

As previously mentioned, the quality data set collected from the monitoring program is sufficient to reasonably describe the hydrogeology of the site and the distribution of the contaminant. However, the location, the composition and the mass of the source cannot be determined from this data nor from the on-site operation reports. Clearly, this vagueness about the source definition adds complexity to its representation through NAS. To address this inconvenient, the NAS tool is herein applied to a two cases involving different source compositions. The aim of this section is to study the effect that different sources have on the dissolution curve. It will also illustrate different approaches to address the source. Predicted source dissolution curves are to be compared to field data.

3.2   Input Parameters

3.2.1   Hydrogeologic Data

The information employs to model the dissolution of the source at the Air Naval Lakehurst site is provided in Table 1.

Table 1. Hydrologic parameters used in NAS simulations

Site Information	Parameter	Unit	Minimum	Average	Maximum
Hydrogeological	Hydraulic Conductivity	ft/year	21,900	27,400	32,900
	Hydraulic Gradient	ft/ft	0.0017	0.002	0.0025
	Weight Percent Organic Carbon	(%)	0.004	0.04	0.008
	Total Porosity	ft^3/ft^3		0.35	
	Effective porosity	ft^3/ft^3		0.25	
Source	Length	ft		20	
	Width	ft		200	
	Contaminated aquifer thickness	ft		10	

3.2.2   Source Characteristics

Three volatile chlorinated plumes exist at Sites I and J of the Naval Air Station Lakehurst; one North plume (NP1) and two South plumes (SP1 and SP2). The monitoring program conducted in this area enable the reasonable determination of the spreading of

all three plumes. However, the characterization of their centerline concentration distribution was partially achieved. At the south plumes, the poor spatial monitoring well distributions around the main flow path hinder both the characterization of the centerline and the application of the analytical strategy previously described. Only the spatial- and temporal- data set gathered from the North plume area provides sufficient information to visualize the migration and degradation of the plume along the centerline. This absence of concentration along the main flow path clearly restricts the application of the NAS software to the two south plumes. Bearing this in mind, this section is to be focused on applying the NAS tool just to the North plume (Figure 3).
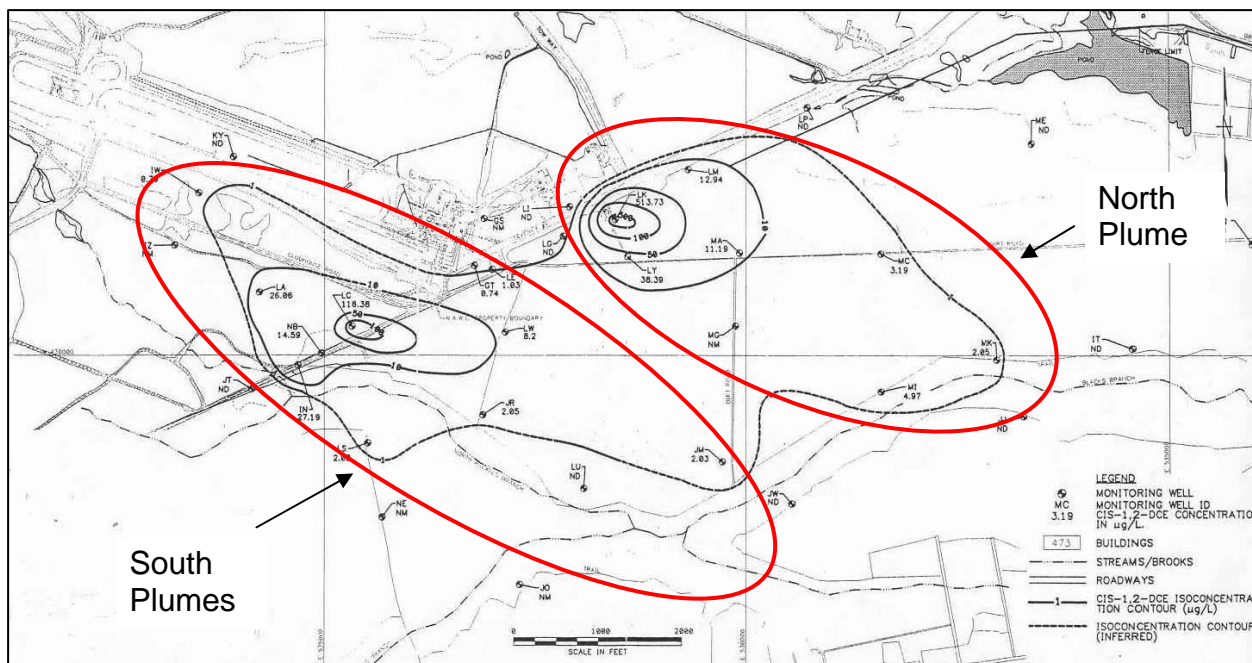
Figure 3. Site map of Areas I and J at NAES Lakehurst, NY. (Ref: Dames and Moore, 1999)

The contaminant source is expected to be spread within the area surrounded by wells LK, LG, and LI. Nevertheless, for modeling purposes, the source is assumed to be situated near well LK. In addition, the concentration profile observed in this well is also assumed to follow the dissolution pattern of the source. This is an important simplification as it will permit the comparison of the field data against the NAS output.

The contamination of the aquifer underneath Site I &J started in the 1960s and carried on until the plume was discovered in the early 1980s. During that 20 years period, a relatively continuous amount of contaminant was incorporated into the groundwater system. To be able to model this contamination problem using NAS, this steady contaminant input has to be expressed as a single contamination event in time. In other words, it is assumed that all the mass dumped in 20 years is released into the environment at a specific time. For this particular transport problem, the contaminant discharge is assumed to occur in the middle of the 20 years period, that is, in 1973. The amount of mass dumped will depend on each simulated case.

The determination of the source dimensions requires the analysis of a set of variables. For instance, the concentration profile at well LK (source well) shows that the average decay trend is rather smooth, which suggests that the source presents a small length (Figure A1). Based on the sensitivity analysis, a reasonable value for this parameter would be 10 ft. On the other hand, the best width source value can be defined when filling the centerline with more concentration data. Since this analytical procedure employs the source width as a parameter, a reasonable first estimation of this parameter is obtained. For this particular transport problem, a 200 ft. width source was imposed.

3.2.3   NAC Analysis – Plume centerline concentrations and redox zonation

Figure 4 shows the location of the wells used to simulate the dissolution of the source at Area I. Note that wells LK and MK are situated in the centerline of the plume and well MA is near it. This last well was chosen to complete the information collected along the centerline by using the analytical strategy described in previous section. The information from well LY and MC, on the other hand, were not transported to the centerline due to their appreciable distance from the main pathway.
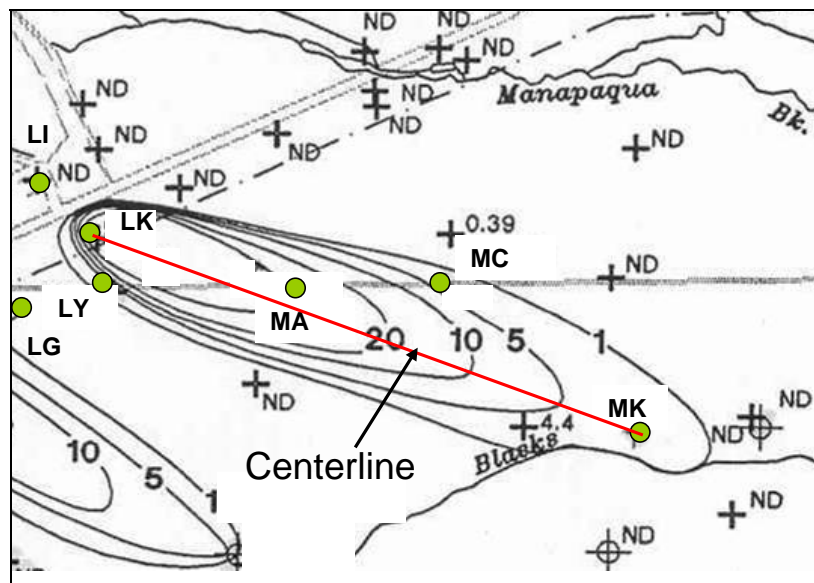
Figure 4. Location of wells used to simulate the transport problem. (Ref: Dames and Moore, 1999)

4.0   Performance Assessment

The NAS tool was employed to predict the decline in aqueous concentration resulting from the dissolution of the NAPL source at a nearby downgradient monitoring well. Source characterization efforts in the field were not extensive and a representative source zone monitoring well was constructed in the aquifer and. Because the composition and location of the source could not be well-defined during the monitoring program, two

hypothetical source compositions were modeled using NAS: 1) single-composite NAPL source (total chlorinated ethenes), 2) multi-constituent NAPL. The objective was to investigate the two different approaches in dealing with the uncertainties in source parameters. Because the source was neither removed nor treated, the comparison between the predicted curve and the existing data is only feasible using a qualitative approach. The calibration of the source parameters was conducted by matching the predicted curve against the field data collected during the first five years period. Later, the resulting source composition was post audited by using the complete data set (8-years data).

For both cases, the predicted curves reasonably match the field data. In regards to the source compositions, the single compound assumption yields to a source mass of 8,000 kg and a mass fraction of 0.05 (Figure 5). TND estimates using NAS are also compared with other methods: a simple data extrapolation method and results of a comprehensive numerical model using the code RT3D. Unlike SEAM3D which employs a mass balance approach to the source term, depleting sources in RT3D must be manipulated by the model users through the implementation of the model input (e.g., time-varying boundary condition).
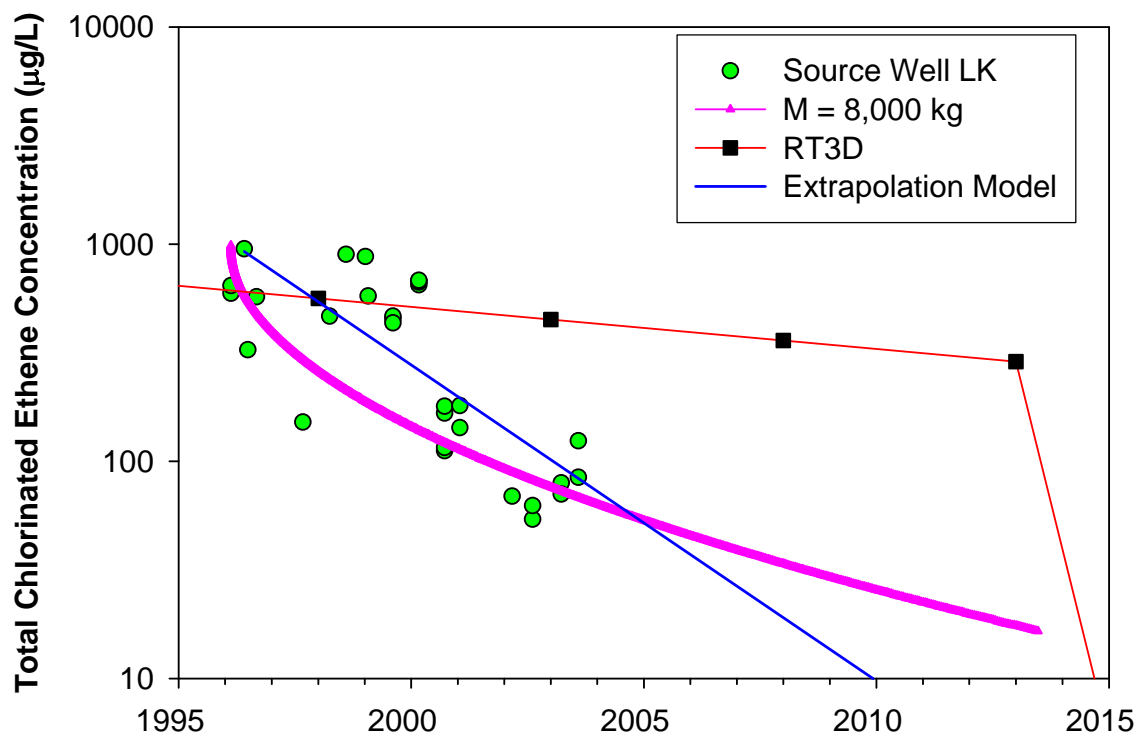
Figure 5. Observed concentrations of total chlorinated ethenes for single-component source models using NAS and RT3D. A data regression is also shown.

In comparison, by including three CVOCs in the NAPL (PCE, TCE, and DCE) a greater source mass (23,000 kg) was required. The total mass fraction of CVOCs is 0.101. This

result suggests that the contaminant source in this site is rather diluted, which is consistent with information gathered from the on-site operation reports that describe the dumped substance as a combination of water-soluble hydraulic fluid, ethylene glycol, trichloroethene, and lubricating oil. Figure 6 reflects a pattern that is usually observed with sources with multiple compounds and shows that the dissolution curves of TCE and DCE can be reasonable reproduced by NAS. The dissolution curves for total chlorinated ethenes in Figure 6 did not match the observed data relative to the curve shown in the single-CVOC NAPL simulation (Figure 5).
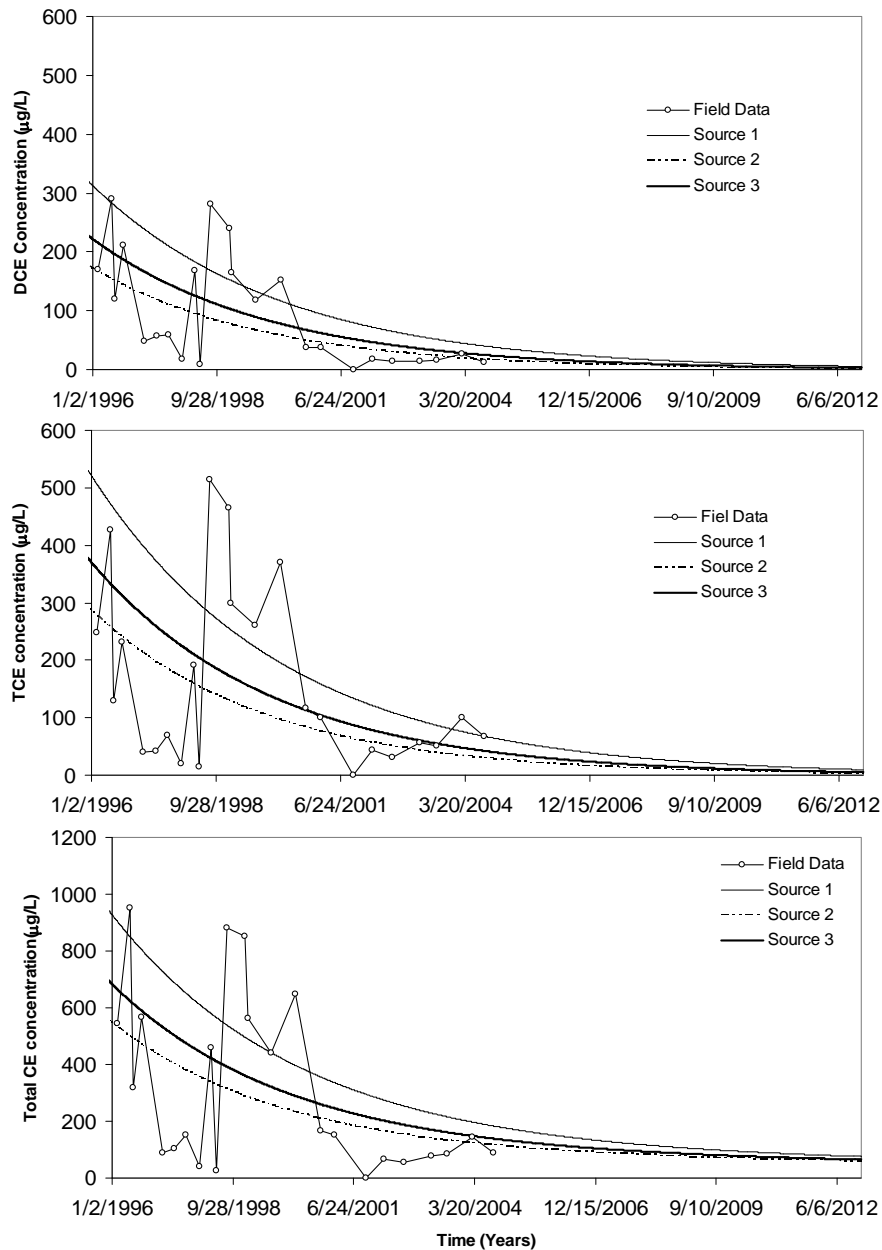
Figure 6. NAS-simulated versus observed concentrations of TCE (top), DCE (middle), and total chloroethenes (bottom) for the multi-component source model.

TORs predicted either using five-years data or the complete data set is rather comparable. For instance, the average TORs for the first case are 54.7 years (Five-years data) and 50.46 years (complete data set). These results further confirm the NAS' capabilities to predict TORs using incomplete data sets.

5.0   References

Dames and Moore. 1999. Final Report – Groundwater Natural Restoration Study, Areas I and J. Contract Number N62472-90-D-1298.

Appendix D: Hill AFB, UT – OU2

Hill AFB, UT – OU2

1.0   Test Site

1.1   History of Operations at the Site

Hill Air Force Base (AFB) in Ogden, Utah has been a working Army and Air Force facility since 1920 and has supported a variety of manufacturing, storage, distribution, airplane maintenance, and missile storage operations. These operations generated and used wastes including chlorinated and non-chlorinated solvents, degreasers, and fuels. In 1987 Hill AFB was placed on the Environmental Protection Agency's National Priority List (NPL) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and both research and remediation have been ongoing since that time. Figure 1 provides a site location map for Ogden Utah and Hill AFB. (URS and Intera: 2003).
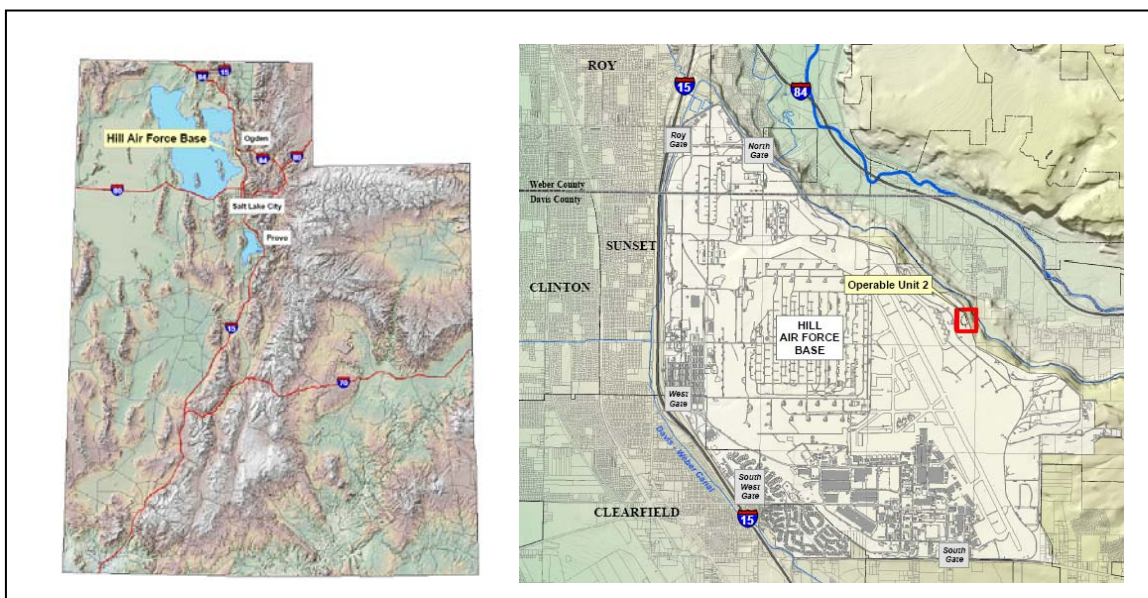
Figure 1. Site Map. (URS and Intera: 2005)

Operable Unit 2 (OU2) is one of several contaminated sites existing within Hill AFB. This site, along the northeastern boundary of the base, was used as a dumping site of an estimated 45- to 50- thousand gallons of chlorinated organic solvents and degreasing agents from 1967 to 1975. The DNAPLs, composed primarily of TCE with smaller amounts of PCE and 1,1,1-TCA, were dumped in unlined trenches and have contaminated the underlying aquifers. (URS and Intera: 2003).

1.2   Present Operation

OU2 is no longer used for any dumping or waste storage. Since 1987, when Hill AFB was placed on the National Priority List, the only activities on this site have been remediation and source recovery operations.

1.3   Selection of Site

This site was selected for this NAS performance assessment because it has several distinguishing characteristics and challenges for applying the general contaminant and groundwater flow equations utilized with NAS. The presence of the low conductivity containment wall around the source area (Figure 2), poses a challenge for predicting future plume concentrations. Most of the source area is surrounded by a containment wall with the assumption that most or all interaction between the contaminant source inside the wall and the plume outside of the wall is interrupted. One region of the source area, however, is not included inside of the containment wall and therefore not all contact between the source area and the plume was severed. Another issue is that the plume flows through two unique aquifer systems with significantly different flow characteristics. Approximately the first 800 feet of the plume downgrading from the source is in the Alpine Formation, with an average horizontal hydraulic conductivity of 2 ft/d, while the remaining length of the plume is in the Weber Formation with an average horizontal hydraulic conductivity of 30 ft/d.

2.0   Site/Facility Characteristics

2.1   Hydrogeology

Three major geologic formations dominate the geology of the OU2 site. Since the dumping ponds are located uphill and the plume expanded downhill, the steeply sloping ground greatly effects groundwater flow direction and velocity. The general simplified aquifer layout is seen in Figure 3. The source area is located in the shallow region of the Provo Formation, but the plume has little contact with this formation so the Alpine and Weber Formations are the main regions considered for plume predictions.

The Provo Formation, the aquifer into which the dumping ponds are located, is composed of unconsolidated silts, sands, and gravels. This formation is located at the topographic high of the contaminated site. The underlying clay aquifer has a complicated topography with a paleochannel eroded into the surface of the clay aquitard. The surface profile of this aquitard is crucial in the understanding of landscape of the source contamination because the DNAPL sinks through the unconsolidated Provo formation and pools in low lying areas of the aquitard. The source area where DNAPL pools were located has been extensively studied, but outside of this area is less known. The Alpine Formation and Weber River Floodplain are located North/Northwest of the source area and have been contaminated through transport.

Figure 2. TCE plume at OU2 showing source area, containment wall and remediation systems.

South   North

Model Column j = 25

492 feet

4400 feet

Provo Formation: K_h = 5 ft/day, K_v = 0.5 ft/day
Alpine Formation: K_h = 2 ft/day, K_v = 0.1 ft/day
Weber River Floodplain: K_h = 30 ft/day, K_v = 3 ft/day
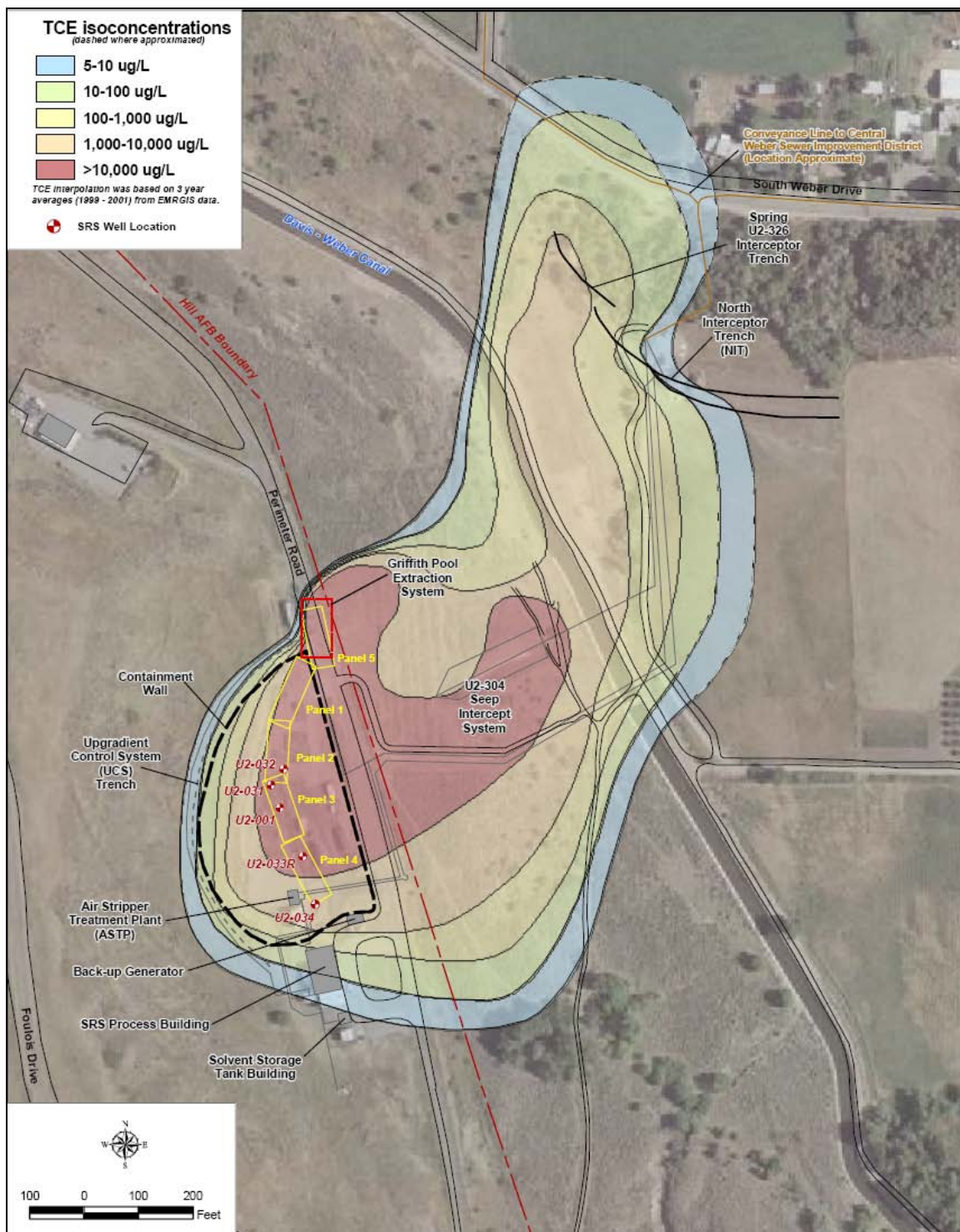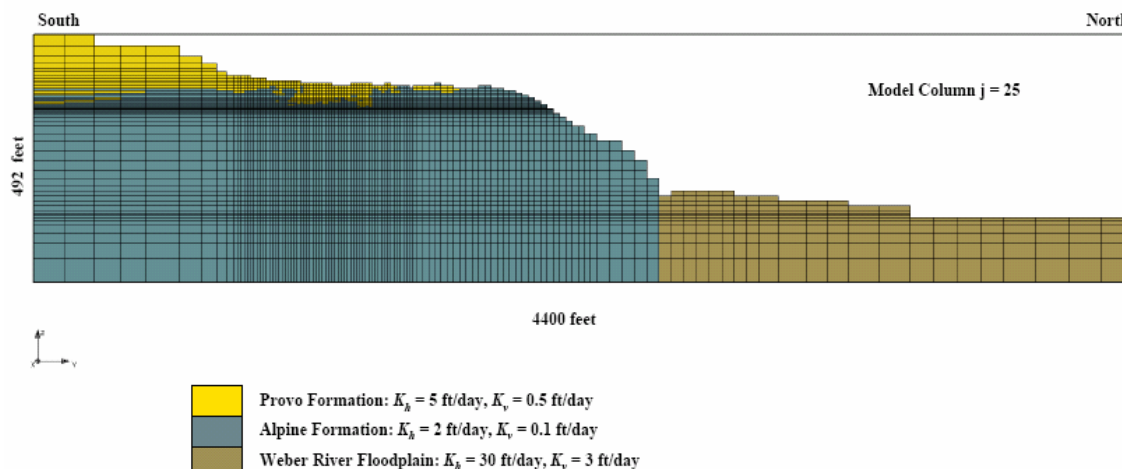
Figure 3. Aquifer Profile of OU2 Plume (Air Force Model: 2005)

2.2   Source and Plume Description

The estimated composition of the source DNAPL is approximately 71% TCE, 9% PCE, 15% TCA, and 5% grease.   The actual source dimensions including the panel outside of the containment wall are 475 feet wide and 25 feet long. Delineation of the plume centerline is of particular importance in selecting appropriate wells to describe the plume concentration along the centerline at various distances downstream. Watertable contours of the aquifer were created using elevation data as in input into ArcMap. The centerline of the plume is delineated as shown in Figure 4.   The contour lines are superimposed onto a location map with estimated TCE concentration contours to provide a reference of scale.

2.3   Past and Current Remediation Strategies

Several remedial actions focusing on the removal of DNAPL and prevention of plume expansion have taken place since this site was added to the EPA's National Priority List. Most remedial effort has been spent in source recovery and remediation in the source zone. Remediation began in 1993 with the implementation of the source recovery system, which includes a groundwater recovery well field and process treatment facility. In 1996 a slurry containment wall reaching to the underlying clay aquitard was constructed to encompass most of the source area and minimize the volume of clean groundwater entering the source zone and to provide a barrier to the movement of contaminants form the source zone to the non-source area.   After the construction of the containment wall, an additional DNAPL pool was discovered outside the wall; this part of the source zone located outside of the containment wall was labeled as panel 5. In 1997, the Griffith Pool DNAPL extraction system, a system of 17 extraction wells installed in and around panel 5, was installed. From 1992 to 2002 several individual experimental DNAPL recovery operations and innovative remediation techniques were implemented in the source area and have resulted in a total DNAPL recovery of approximately 43,823 gallons, or approximately 90% of the estimated initial source volume.

Figure 4. Centerline of Plume.

Interceptor trenches were constructed to capture contaminated groundwater flowing through the aquifer; this water is pumped to a treatment facility (Fig. 2).   The North Interceptor trench, which was constructed near the leading edge of the contaminated groundwater plume, was intended to intercept the groundwater with TCE concentrations greater than 5- ppb before it spread contamination further downgradient. The Spring U2-326 Interceptor Trench was built two years after the construction of the North Interceptor Trench to extend the region of groundwater interception in the northwest direction. The Spring U2-304 Seep Interceptor Trench was installed to collect groundwater from the center of the plume, but this trench has remained dry for most of its operational life.   A total of three trenches have been constructed but are fairly shallow in relationship to the depth of the aquifer and their impact of groundwater flow and contaminant interception is unknown.

2.4   Groundwater Flow and Transport Modeling – Previous work

In March 2005 a comprehensive flow and transport numerical modeling study was conducted (URS 2005).

3.0   Demonstration Approach

3.1   Modeling Objective

Using data ranging from 1996 to the present, the remediation of contaminants in the plume from the OU2 site is studied and evaluated for trends and predictability of future developments. The main goal of this work is to determine to what degree NAS can accurately predict and follow the trends of groundwater concentration with time along the length of the plume as the result of changes to the source zone mass flux resulting from the construction of a containment wall.

3.2   Input Parameters

3.2.1   Hydrogeologic Data

Hydraulic conductivity values for separate hydrostratigraphic units at OU2 are shown in Table 1. As reported in a previous study, "Lack of information regarding the conductivity of sediment types other than the most coarse-grained channel fill constitutes a substantial data gap in the conceptual understanding of OU2" (URS and Intera: 2005).

Table 1.— Hydraulic conductivity at OU2

Zone	Hydraulic Conductivity	
	Horizontal (ft/d)	Vertical (ft/d)
Provo Formation	5	0.5
Alpine Formation	2	0.1
Weber River Floodplain	30	3.0
Panel 5	5	0.008

Hydraulic gradient varies along the length on the plume and is dependent on a number of factors including hydraulic conductivity, topography, and manmade alterations in the subsurface such as the low conductivity containment wall and interceptor trenches. The gradient is particularly important to examine near the containment wall that surrounds the source area to understand the impact of the wall on groundwater flow. If gradient here is understood, it can be used to analyze contaminant concentration data to find remediation trends.

Seven wells with groundwater elevation data close to the front edge of the containment wall are used to create 1-ft contours. A groundwater mound forms causing a gradient towards the wall resulting in an upstream gradient for some distance before resuming a downward gradient

downstream for the remainder of the plume when wells U2-117, 659, 640, 657, 023, 018, and 085 are used as shown in Figure 7 (left). However, if well U2-085 is discounted, an average gradient downstream is established as shown in Figure 7 (right). These contour plots were created using the GIS program ARC Map's contouring tool. The gradient along the centerline of the plume is calculated using the groundwater contours presented in Figure 5. The different approaches for calculating the horizontal hydraulic gradient and results are listed in Table 2. Weight percent organic carbon, the porosity, and the effective porosity values listed in Table 3.

Table 2. Hydraulic Gradient along Plume Centerline.

	Distance along Centerline of Plume	Direction of flow	Hydraulic Gradient (ft/ft)	Assumption
First 150 feet of plume	First 90 feet (0- 90 feet)	Towards Source	0.047	Assuming initial inward gradient at wall
	Next 60 feet (90- 150 feet)	Downstream	0.23	
	OR			
	First 150 feet (0- 150 feet)	Downstream	0.08	Assuming no inward gradient at wall
	AND			
Remainder of plume	Next 370 feet (150 – 520 feet)	Downstream	0.22	
	Next 610 feet (520 to 1130 feet)	Downstream	0.07	
	Next 320 feet (1130 – 1450 feet)	Downstream	0.22	

3.2.2 Source Characteristics

The containment wall surrounding most of the source is approximately 395 feet wide and 220 long. Interaction between the plume and the source is minimized due to the containment wall, which is simulated with a source reduction estimate in the TOS analysis.

Table 3. Aquifer Parameters

	Weight percent organic carbon	Porosity	Effective Porosity
Alpine Formation	.005-.03	20%	No estimate
Weber River Floodplain	.001-.002	30%	No Estimate
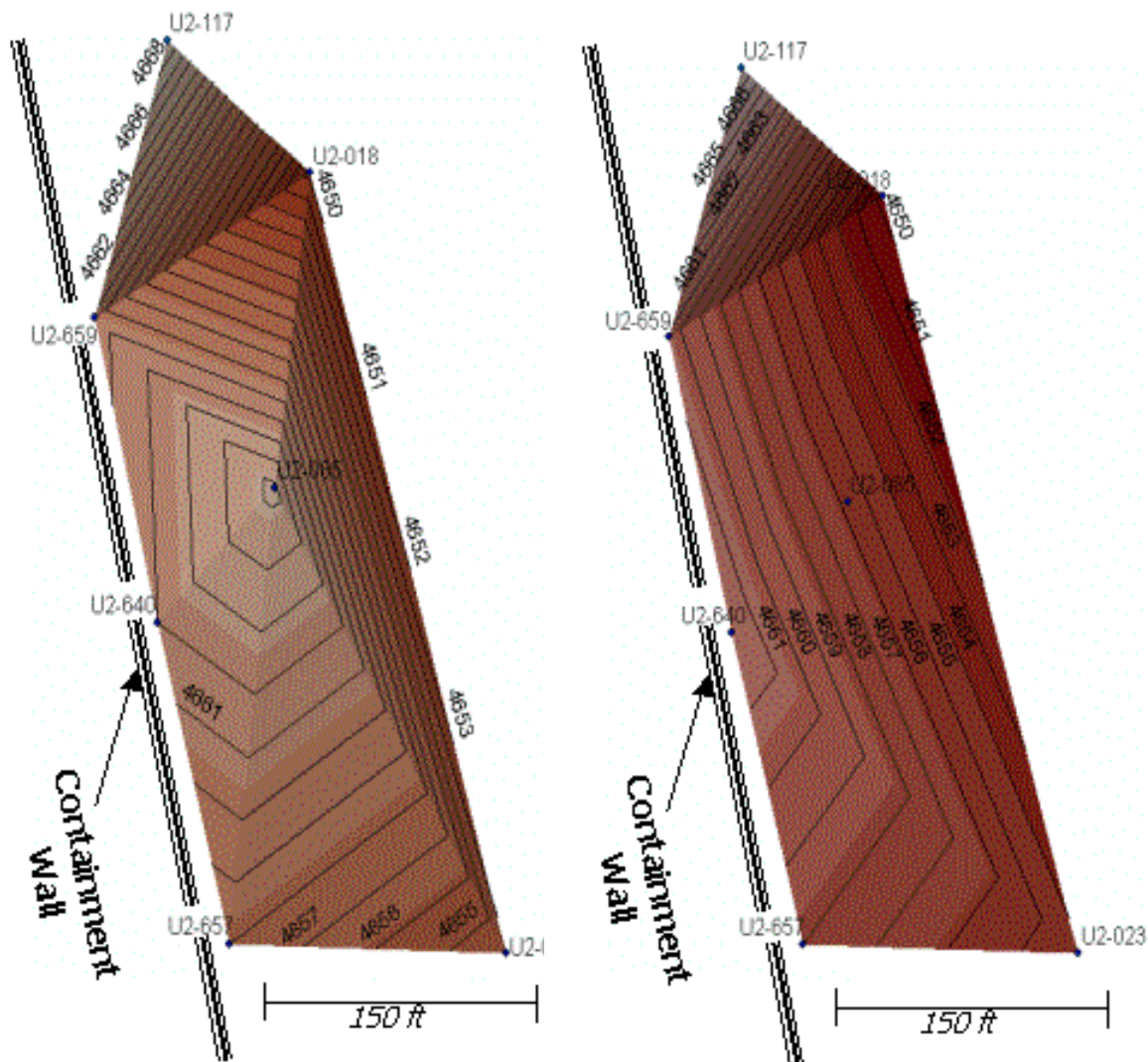
Figure 7. Gradient at near the containment wall including Well U2-085 in the analysis (left) and discounting Well U2-085 (right).

3.2.3 NAC Analysis – Plume centerline concentrations and redox zonation

Figure 8 provides a schematic of the wells along the centerline of the plume, their relative distances along the length of the plume, the formations in which they are located, and the associated hydraulic parameters. Well U2-085 was set as the first monitoring well because this well was a local high point of groundwater elevation where water in the region between the containment wall and the well flows towards the wall and groundwater in the region beyond this well flows downgradient in the direction of the regional groundwater flow.
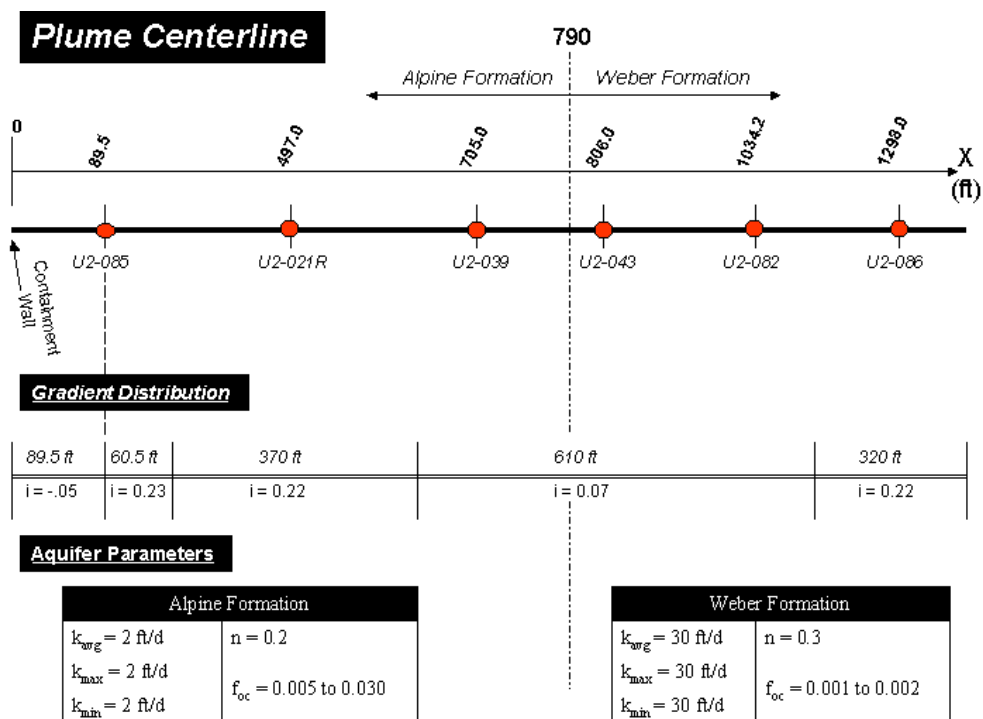
Figure 8. Plume Centerline Wells, Gradient Distribution, and Aquifer Parameters.
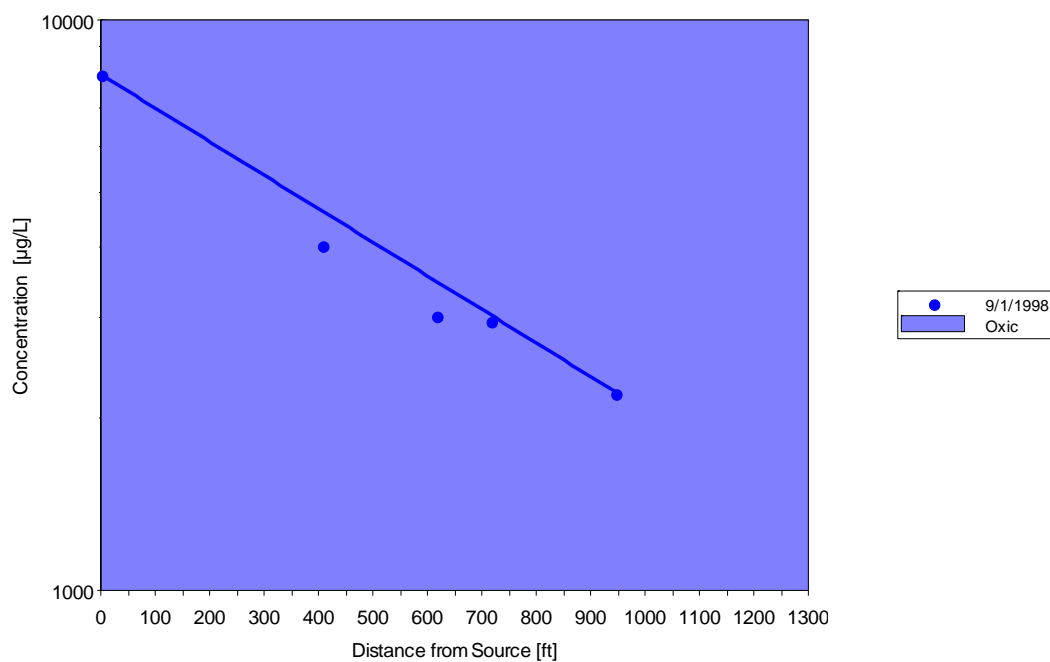
Figure 9. TCE Concentration along Centerline of Plume.

4.0   Performance Assessment

Scenario A – Simulation of C vs time using Alpine Formation input parameters

In this scenario, the groundwater velocity is based on hydrogeological parameters found in the Alpine Formation only. The contaminant data from September 1998 and the redox data from January 2002, as well as the Alpine Formation parameter values presented in Table 4 was input.

Table 4. Transport Parameters for Scenario A

	Groundwater Velocity (ft/d)	TCE Retardation Factor	Contaminant Velocity (ft/d)
Maximum	1.83	32.7	0.81
Average	1.83	7.56	0.24
Minimum	1.83	2.27	0.056

As portrayed in Figure 10, TCE concentration versus time at Well U2-21R, which is the closest downstream point with known data in this formation, is match to the observed data by estimating the TCE source concentration (3,467 µg/L). At the monitoring well immediately downgradient of the source (Well U2-085), the TCE concentration did not increase following construction of the wall, but instead tended to fluctuate with an increasing trend over time. This is likely due to the stagnation of groundwater immediately downgradient of the wall, as shown in Fig. 7 (left). The date of source reduction is set at June, 1996 to represent the date which the containment wall was constructed.

Figure 11 depicts concentration versus time at two monitoring wells further downgradient. Although Well U2-039 (top) is closer to the source than Well U2-043 (bottom), NAS-generated TOS estimates are superior at the more distant well. This is most likely due to the meandering configuration of the plume and changes in the flow pattern resulting from the construction of the slurry containment wall.

Scenario B – Simulation of C vs time using Weber Formation input parameters

Table 5 lists transport parameters used in Scenario B, which is based on the hydrogeologic parameters associated with the Weber Formation (later portion of the plume). The TCE source concentration from Scenario A was used in this simulation. Figure 12 shows that this parameter set provided an inferior fit to the observed data at Well U2-21R.

Table 5. Transport Parameters for Scenario B

	Groundwater Velocity (ft/d)	TCE Retardation Factor	Contaminant Velocity (ft/d)
Maximum	8.75	32.7	3.85
Average	8.75	7.56	1.16
Minimum	8.75	2.27	0.27

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Source Reduction and Time of Stabilization

1. Enter the distance from the contaminant source to the nearest downgradient Point of Compliance (POC).

Distance to POC[ft]   407.0   U2-021R

2. Enter the Regulatory Compliance Concentration (RCC) at the Point of Compliance (POC) to determine the required Target Source Concentration (TSC), or enter the TSC after source reduction to determine the Concentration at the POC.

| | | Source Reduction | | | Time of Stabilization [years] | | | | | |
| | RCC | | Conc [µg/L] | | Breakthrough Time | | | Time to Equilibrium | | |
Contaminant	[µg/L]	Well	Current	Target	Maximum	Average	Minimum	Maximum	Average	Minimum
Total Chl. Eth.	160.1	1	8091	276	6.3	2.6	1.1	13.4	7.1	3.4
PCE	1.5	1	74	4	7.9	3.5	1.5	13.2	7.3	4.0
TCE	2000.0	1	8017	3467	6.2	2.6	1.1	13.3	7.1	3.4
cis-DCE	12.5	2	209	POC is closer than Source Well						
Vinyl Chl.		Insufficient Data								

Close   Graph

TCE at Well U2-021R at 407.00 ft
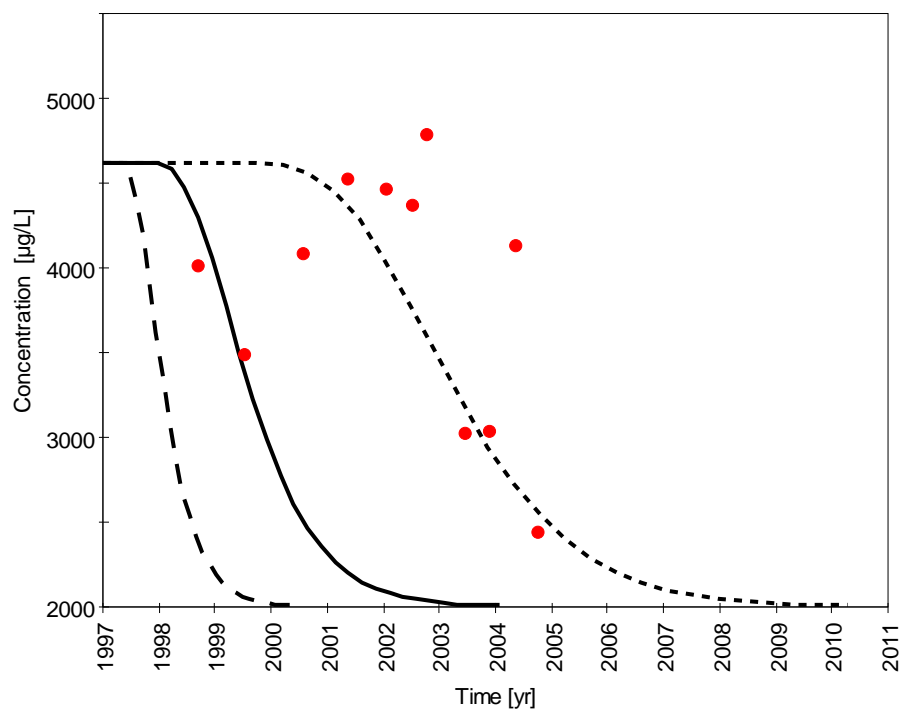
Figure 10. Time of Stabilization Estimates for Scenario A using Well U2-021R.
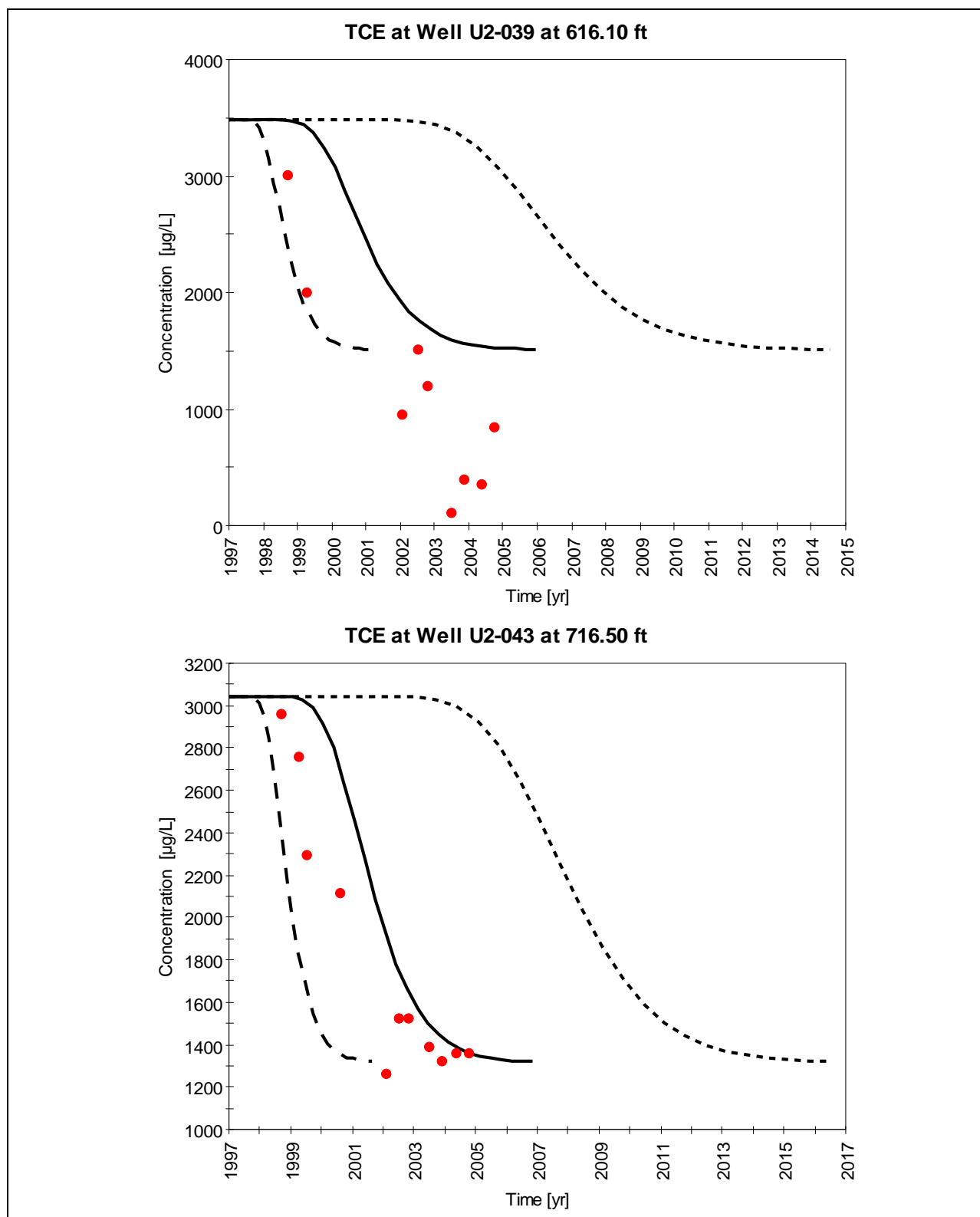
Figure 11. TOS Estimates for Wells Downgradient of U2-021R for Scenario A.

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Source Reduction and Time of Stabilization

1. Enter the distance from the contaminant source to the nearest downgradient Point of Compliance (POC).

Distance to POC[ft] 407.0   U2-021R

2. Enter the Regulatory Compliance Concentration (RCC) at the Point of Compliance (POC) to determine the required Target Source Concentration (TSC), or enter the TSC after source reduction to determine the Concentration at the POC.

| | | Source Reduction | | | Time of Stabilization [years] | | | | | |
| | | | Conc [µg/L] | | Breakthrough Time | | | Time to Equilibrium | | |
Contaminant	RCC [µg/L]	Well	Current	Target	Maximum	Average	Minimum	Maximum	Average	Minimum
Total Chl. Eth.	160.1	1	8091	276	1.3	0.5	0.2	2.8	1.5	0.7
PCE	1.5	1	74	4	1.7	0.7	0.3	2.8	1.5	0.8
TCE	2000.0	1	8017	3467	1.3	0.5	0.2	2.8	1.5	0.7
cis-DCE	12.5	2	209	POC is closer than Source Well						
Vinyl Chl.		Insufficient Data								

Close   Graph

Total Chl. Eth. at Well U2-021R at 407.00 ft
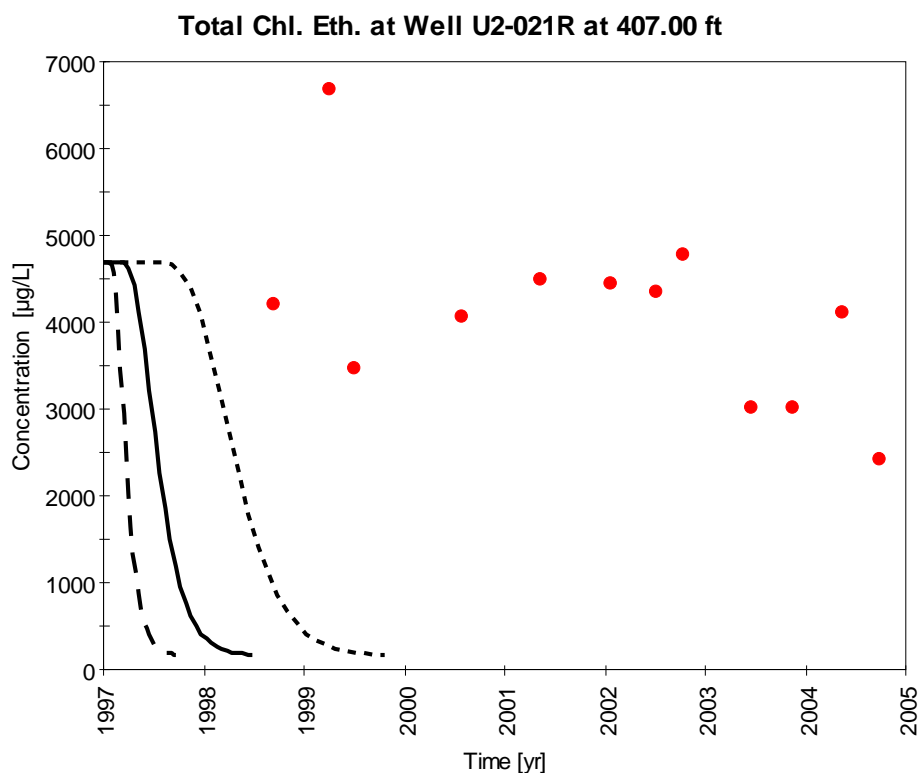
Figure 12. Time of Stabilization Estimates for Scenario B using Well U2-021R.

Scenario C – Simulation of C vs time using spatially-averaged hydraulic gradient

In the last of 3 scenarios, the hydraulic conductivity from Scenario A (Alpine Formation) was used again but the hydraulic gradient was averaged over space to adjust for perturbations created by the recharge mound directly downgradient of the slurry wall. Table 6 lists the range in contaminant velocity values based on a more representative horizontal hydraulic gradient (0.07).

Table 6. Transport Parameters for Scenario C

	Groundwater Velocity (ft/d)	TCE Retardation Factor	Contaminant Velocity (ft/d)
Maximum	0.583	32.7	0.257
Average	0.583	7.56	0.077
Minimum	0.583	2.27	0.018

The results of Scenario C are shown for Well U2-21R and the downgradient monitoring wells in Figures 13 and 14, respectively. Similar to the results of Scenario A, the NAS-simulated TOS results match the observed data at Wells U2-043 and -21R, but an inferior match is apparent at Well U2-039.

5.0   References

URS and Intera. 2003. Conceptual Model Update for Operable Unit 2 Source Zone: Hill Air Force Base, Utah. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas and Environmental Management Division, Hill Air Force Base, Utah. 152 p.

URS and Intera. 2005. Flow and Contaminant Transport Model: Operable Unit 2, Hill Air Force Base, Utah. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas and Environmental Management Division, Hill Air Force Base, Utah. 152 p.

Natural Attenuation Software

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Source Reduction and Time of Stabilization

1. Enter the distance from the contaminant source to the nearest downgradient Point of Compliance (POC).

Distance to POC[ft] 407.0   U2-021R

2. Enter the Regulatory Compliance Concentration (RCC) at the Point of Compliance (POC) to determine the required Target Source Concentration (TSC), or enter the TSC after source reduction to determine the Concentration at the POC.

| | | Source Reduction | | | Time of Stabilization [years] | | | | | |
| | | | Conc [µg/L] | | Breakthrough Time | | | Time to Equilibrium | | |
Contaminant	RCC [µg/L]	Well	Current	Target	Maximum	Average	Minimum	Maximum	Average	Minimum
Total Chl. Eth.	160.1	1	8091	276	19.6	8.2	3.4	42.0	22.3	10.8
PCE	1.5	1	74	4	24.8	11.1	4.8	41.4	23.1	12.6
TCE	2000.0	1	8017	3467	19.6	8.2	3.4	41.7	22.2	10.8
cis-DCE	12.5	2	209	POC is closer than Source Well						
Vinyl Chl.		Insufficient Data								

Close   Graph
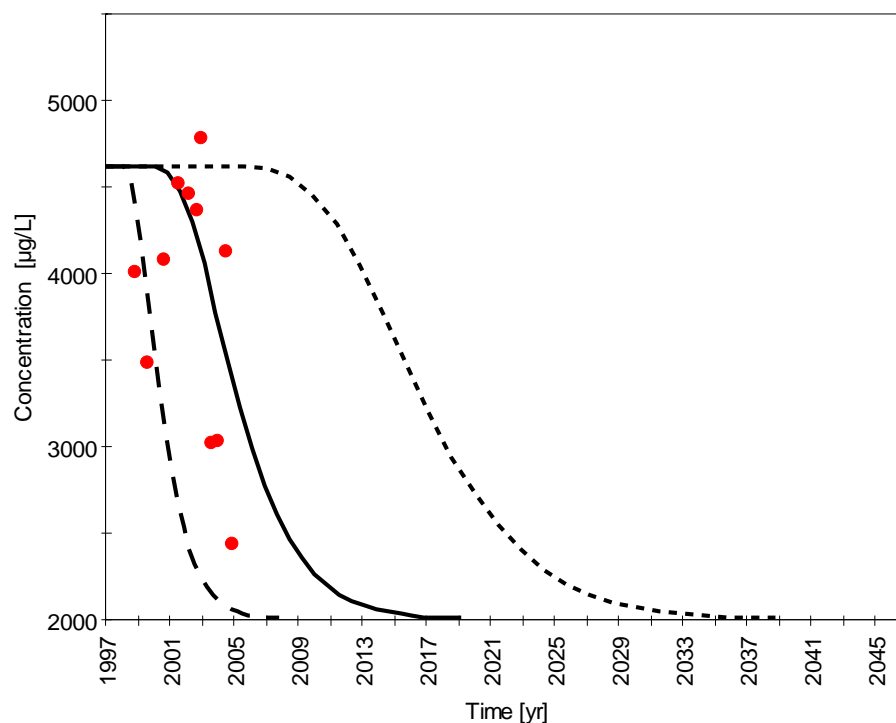
TCE at Well U2-021R at 407.00 ft

Figure 13. Time of Stabilization Estimates for Scenario C using Well U2-021R.
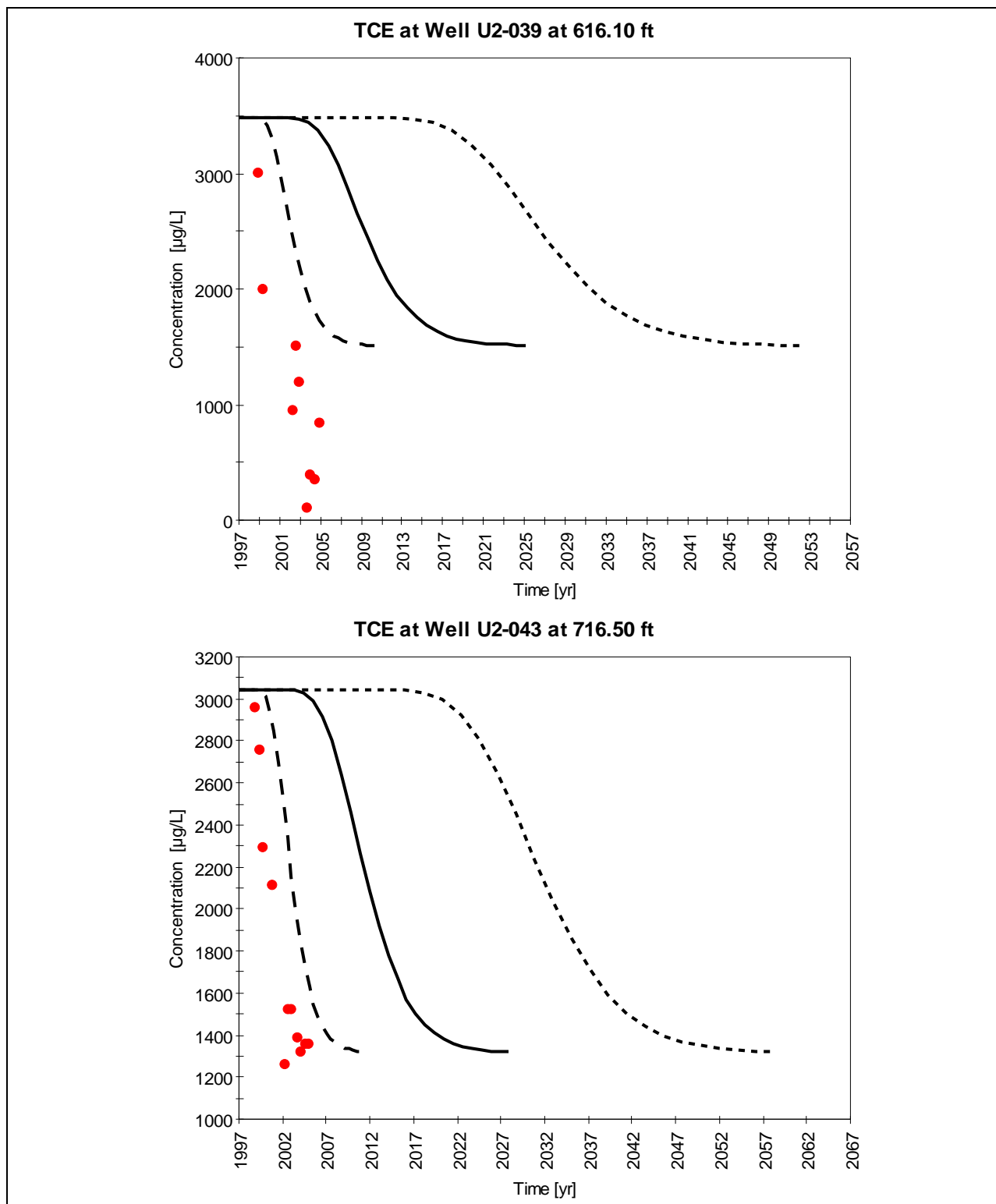
Figure 14. TOS Estimates for Wells Downgradient of U2-021R for Scenario C.

Appendix E: NSB Kings Bay, GA – Site 11

NSB Kings Bay, GA – Site 11

1.0   Test Site

1.1   History of Operations at the Site

Naval Submarine Base (NSB) Kings Bay encompasses more than 16,000 acres near the Georgia-Florida border in Camden County, GA. Commissioned in 1978, the base originally served as a forward refit site for submarine squadrons. In 1980 the base was designated as U.S. Atlantic Fleet home port to the next generation of ballistic submarines. NSB Kings Bay also maintains and operates administration and personnel support facilities. Site 11 is the location of a former 25-acre landfill at NSB Kings Bay, known as the Old Camden Country landfill that was operated by the county during the mid-1970s to 1980. A variety of wastes from the local Kings Bay community and the Navy were disposed of in the landfill, including solvents and municipal waste, in unlined trenches. In the 1990's a chloroethenes plume (Figure 1) was discovered to be migrating from a PCE source zone (Chapelle et al. 2005).

1.2   Present Operation

The landfill no longer receives solid or hazardous waste from the base or county and has been closed since 1981.

1.3   Selection of Site

NSB Kings Bay Site 11 is presently the well-documented site where source remediation was successful in reducing the size of a plume. The geochemistry of the ground-water system and the contaminant plume is described in detail by Chapelle and Bradley (1998). Chapelle et al. (2005) described a 6-yr post-treatment monitoring program at the downgradient monitoring with particular focus on VC concentration in the plume.

2.0   Site/Facility Characteristics

2.1   Hydrogeology

NSB Kings Bay is located in the Atlantic Coastal Plain. The study site is underlain by marginal marine sediments of barrier island and back-barrier lagoon origin. The most permeable sands underlying the site are present between depths of 10 and 13 m below ground surface (bgs). This permeable zone is underlain and overlain by finer-grained sands and clays of back-barrier lagoon origin characterized by lower hydraulic conductivity. Hydraulic conductivity of the permeable zone is 3 m/d based on aquifer tests and lithologic data. An organic-rich layer of soil overlying the aquifer at depth of ~3 to 5 m bgs has an important role in natural attenuation by removing

DO from recharge waters. Ground water velocity based on tracer data ranges from 10 to 20 m/yr (Chapelle et al. 2005).

Figure 1. Chloroethene plume and monitoring wells at Site 11, NSB Kings Bay. (Source: Chapelle, F.H., P.M. Bradley, and C.C. Casey, 2005. Behavior of a chlorinated ethene plume following source-area treatment with Fenten's reagent. Ground Water Monitoring and Remediation, 25(2): 131-141).

2.2   Source and Plume Description

Source zone investigations conducted in the mid to late 1990s revealed a 120-ft long by 40-ft wide PCE source with the characteristics of a DNAPL at a depth of 30 to 40 feet bgs. PCE concentration in source zone ground water samples ranged 3.5 to 8.5 mg/L. A plume of CVOCs flowed in the ground water toward a residential area located outside the facility to the west of the landfill. Reductive dechlorination promoted by reducing conditions in the aquifer resulted in biotransformation of PCE and TCE to cis-DCE and VC along the ground water flowpath. Redox

processes favoring anaerobic direct oxidation at the toe of the CVOC plume resulted in the oxidation of VC to carbon dioxide (Chapelle and Bradley 1998).

2.3   Past and Current Remediation Strategies

Following a RCRA Facility Investigation (RFI) conducted in the early 1990's, pumping wells were installed to exert hydraulic control on the plume as an interim measure. Direct-push sampling in the suspected source zone detected two adjacent sources of PCE in the vicinity of well KBA-34 where the historically-highest concentrations of PCE (3,500 – 9074 μg/L) were detected (Chapelle and Bradley 1998). Beginning in 1998, source zone engineered remedial action (ERA) consisted of in situ chemical oxidation using Fenton's reagent followed by injection of emulsified vegetable oil. The latter component was designed to promote a return of redox conditions favorable to reductive dechlorination so that MNA could be employed as the final remediation step. The successful removal of the PCE source and subsequent plume reduction has been documented (Chapelle et al. 2003; 2005).

2.4   Groundwater Flow and Transport Modeling – Previous work

Chapelle and Bradley (1998) describe the application of a one-dimensional analytical solution to determine the level of source zone remediation (decrease in the groundwater contaminant concentration) to meet the remedial action objective of shrinking the plume to MCL at the facility boundary.

3.0   Demonstration Approach

3.1   Modeling Objective

Site 11 provides an excellent opportunity to compare NAS simulations of TOS at monitoring wells downgradient of the source zone using groundwater data collected over a six-year period. TOS simulations will be compared with observed data using first parameter estimates based on pre-remediation data and then using parameter estimates based on data collected after source zone remediation.

3.2   Input Parameters

3.2.1 Hydrogeologic Data

Prior to source treatment, Chapelle and Bradley (1998) estimate the range in the groundwater velocity (0.014 to 0.23 m/d) using Darcy's Law and using the range in field-measured hydraulic conductivity, horizontal hydraulic gradient (0.006), and an estimate of effective porosity (0.25). Retardation factors for PCE, TCE, cis-DCE, and VC (6.50, 2.90, 1.98, and 1.86, respectively) are calculated based on the fraction of organic carbon (0.0019). Because PCE rapidly depleted along the groundwater flow path and was absent from the downgradient monitoring wells (KBA-13A

and USGS-5) in the pretreatment plume, the range in the estimated composite retardation factor for total chlorinated ethenes is 1.86 to 2.90. The resulting range in the contaminant velocity (0.0050 to 0.12 m/d) shows that the maximum and minimum values vary by a factor of 25. The other parameters are based on the results of the site investigation and the pre-treatment plume. The source width (20 m) is based on the results of the source zone investigation.

4.0   Performance Assessment

Simulation of C vs time using pre-remediation parameter estimates

Figure 2 shows a comparison of observed data at KBA-13A ($L = 49$ m) with two sets of solutions for the reduction in the total chlorinated ethene concentration versus time; one solution set represents the maximum estimated groundwater velocity (0.23 m/d) using the range of retardation factors (1.89-2.90) and the other represents the initial minimum estimated contaminant velocity range. Results using the initial estimated input parameters show an underestimate of the actual concentration time trend and the time of stabilization (Table 1). Only when the retardation factors are increased for each set to 35 and 3.8 for the initial maximum and minimum estimates, respectively, does a best-fit of the predicted to the observed data occur and *RMS* values are at a minimum (41 and 32, respectively). These results further demonstrate that the uncertainty in predicting the time trend at a POC is directly associated with the uncertainty in determining the contaminant velocity.
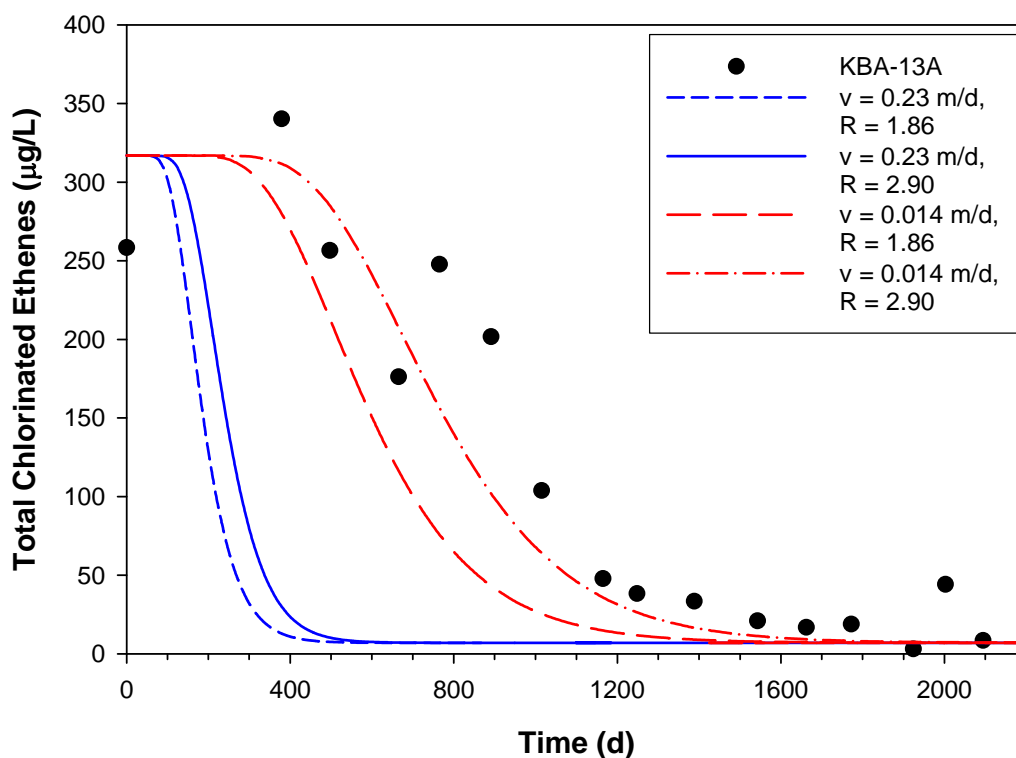
Figure 2. Observed (circles) and predicted total chlorinated ethene concentrations at well KBA-13A showing the full range of groundwater velocity and retardation factor values based on initial estimates made prior to the source zone treatment.

Table 1. Hydrologic parameters used in NAS simulations

Input Parameter and Time of Stabilization for Well KBA-13A					
v (m/d)	λ (d^{-1})	R	v_c (m/d)	t_s (d)	*RMS*
Initial Max. Est.					
0.23	0.0165	1.89	0.124	490	143
		1.98	0.116	500	142
		2.90	0.079	580	140
Initial Min. Est.					
0.072	0.0052	1.89	0.039	1550	70
		1.98	0.036	1600	66
		2.90	0.025	1860	41
Tracer-based					
0.055	0.0039	1.89	0.029	2050	37
		1.98	0.028	2110	34
		2.90	0.019	2460	41

Simulation of C vs time using post-remediation parameter estimates

A tracer-based value of the groundwater velocity is obtained from the breakthrough curve in the sulfate concentration at KBA-13A presented in Chapelle et al. (2005). A pulse of sulfate was observed in several observation wells resulting from the use of ferrous sulfate with the Fenton's reagent in the source zone and subsequent transport with the natural gradient. The resulting velocity (0.055 m/d) is simply the travel distance between KBA-34 and KBA-13A divided by the travel time (895 d) to the peak sulfate concentration. The results using the tracer-based velocity estimate in Figure 3 and Table 1 show improved agreement between the observed and calculated concentration trend when compared to the initial estimates. However, an improved velocity estimate is only available when the 6-yr monitoring program is approximately 40% complete because the sulfate breakthrough at KBA-13A was not sufficiently ahead of the decrease in the concentration of total chlorinated ethenes to allow an earlier updated prediction. For the tracer-based velocity the minimum value of *RMS* (30) is achieved for a retardation factor of 2.28. The TOS estimate is 2,200 days, which is consistent with observed concentration data between the source and KBA-13A.

Concentration versus time at USGS-5 simulated with the input parameter set for well KBA-13A clearly fails to represent the observed monitoring data (Figure 4). Specifically, the simulated decrease in concentrations begins at $t \approx 600$ d, well before the start of the observed decline ($t \approx 1,400$ days), indicating that the simulated contaminant velocity is too large. Analysis of the

sulfate breakthrough curve at well USGS-5 resulted in a groundwater velocity of 0.040 m/d. The discrepancy in this result and the tracer-based groundwater velocity at well KBA-13A (0.055 m/d) may reflect the proximity of wells USGS-5 and KBA-13A to the extraction wells and source-area injection wells, respectively. The impact of a reduction in groundwater velocity caused by cessation of pumping is more likely to impact observations at well USGS-5 relative to well KBA-13A, whereas the impact of a temporal increase in velocity induced by injection of Fenten's reagent is more likely to be observed at well KBA-13A. An improved match between the observed and simulated concentration reduction over time is noted using lower values of the groundwater velocity (0.040 m/d) and the decay coefficient (0.0029 d^{-1}). The latter parameter is modified to maintain the same initial condition (120 µg/L) as the previous case. TOS estimates are 2,700 and 3,600 days, respectively.
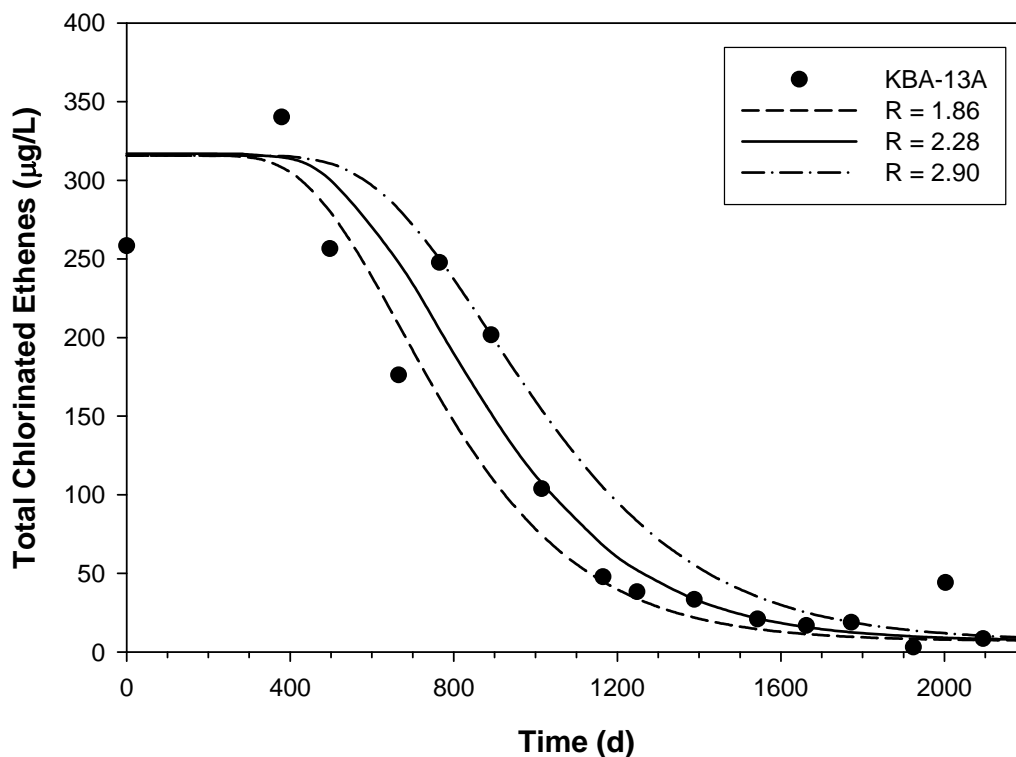
Figure 3. Observed (circles) and predicted total chlorinated ethene concentrations at well KBA-13A using groundwater velocity ($v = 0.055$ m/d) determined from the breakthrough of sulfate and the range of retardation factors, including the case ($R = 2.28$) where the residual error is minimized.

Two additional simulations are presented in Figure 8 using the tracer-based groundwater velocity at USGS-5. The simulation that best matches the complete fit of observed data has a *RMS* value of 19 compared to 37 and 29 for the previous simulations. However, a retardation factor of 4.00 is required to capture the concentration decline for $t > 1,400$ days. As a consequence, the best-fit simulation produces the largest estimate of t_s (4,200 days). In the final case, the observed

concentration at well USGS-5 immediately prior to source treatment (as opposed to a best-fit match of the pretreatment plume) is exactly matched by decreasing the decay coefficient (0.0024 d^{-1}) relative to the other simulations. Although the simulated result does not match the observed data trend for $t < 1,800$ days, the latter part of the concentration decline is captured by the solution with the least error relative to other parameter sets. The resulting estimate for time of stabilization is 3,700 days.
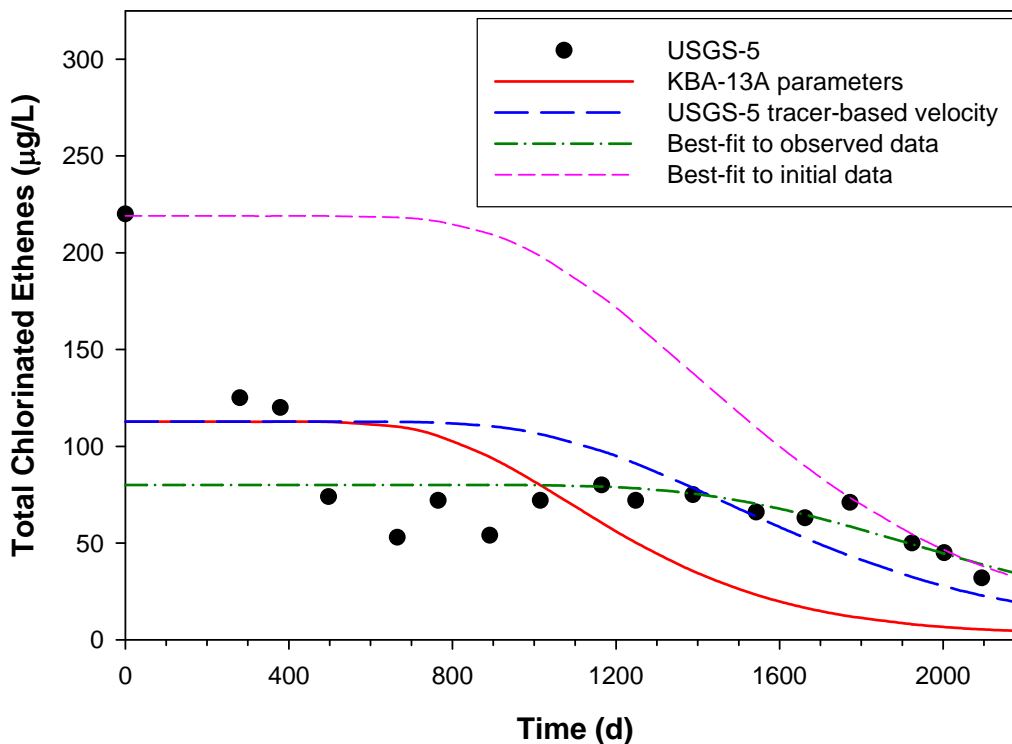
Figure 4. Observed (circles) and predicted total chlorinated ethene concentrations at well USGS-5 for four input parameter sets: (1) best-fit input parameters from Figure 3; (2) velocity using tracer breakthrough at USGS-5 (0.040 m/d); (3) best-fit to the complete data set; (4) best-fit to the initial concentration data.

5.0   References

Chapelle, F.H. and P.M. Bradley. 1998. Selecting remediation goals by assessing the natural attenuation capacity of ground-water systems. *Bioremediation Journal* 2, nos. 3 and 4: 227-238.

Chapelle, F.H., M.A. Widdowson, J.S. Brauner, E. Mendez III, and C.C. Casey. 2003. Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation. USGS WRIR 03-4057.

Chapelle, F.H., P.M. Bradley, and C.C. Casey. 2005. Behavior of a chlorinated ethene plume following source-area treatment with Fenten's reagent. *Ground Water Monitoring and Remediation* 25, no. 2: 131-141.

Appendix F: NAS Cecil Field, FL – Site 3

NAS Cecil Field, FL – Site 3

1.0   Test Site

1.1   History of Operations at the Site

Naval Air Station Cecil Field (NASCF) is a former naval air station established in 1941 that provided facilities, services, and material support for naval operations. The facility is located in southwestern Duval County, Florida within the Jacksonville city limits. The main facility occupies 9, 516 acres. Some of the operations at the facility included operation of fuel storage facilities as well as intermediate level aircraft maintenance. In 1989 the installation was placed on the NPL due to the potential environmental threat associated with waste sites located at the facility (ABB ES, 1997).

Site 3 is a vacant area located approximately 3,500 feet west of the end of an active aircraft runway on the western perimeter of NASCF (Figure 1). It was an Oil and Sludge Disposal Pit that was used to dispose of liquid wastes and sludge. The period when disposal operations began at the site is uncertain. A review of aerial photographs during the Remedial Investigation (RI) (ABB ES, 1996) suggested the area was not disturbed prior to 1960 and records detailing this disposal activity are absent. However, base disposal operations were expected to have begun during the late 1950's to the early 1960's and ceased by 1975. Waste products potentially disposed at the site include fuels, oils and solvents. Some of the estimated (Envirodyne Engineers, 1985) volumes of wastes included: 440,000 gallons of petroleum-oil-lubricants, 110,000 gallons of spent solvents and over 300,000 gallons of other liquid wastes. Wastes were reportedly drained into the pit from portable bowsers or 55-gallon drums and allowed to evaporate and/or seep into the ground. The liquid wastes were periodically burned by the NASCF fire department when the wastes reached the top of the shallow pit (ABB ES, 1996). Investigation of shallow ground water contaminated from these operations was determined to exceed risk-based criteria and require remediation.

1.2   Present Operation

NASCF is a closed naval air station that was part of the 1993 and 1995 Base Realignment and Closures (BRAC). The base officially closed September 30, 1999. Most of the property has been transferred to the city of Jacksonville, Florida and has undergone various reuse alternatives. Vegetation covers much of Site 3, which includes thick shrubs and small trees. There are no residential, commercial or industrial activities associated with the site and development is expected to be limited due to its proximity to the flight line. Flight operations are part of the planned reuse of the facility and are expected to continue indefinitely.
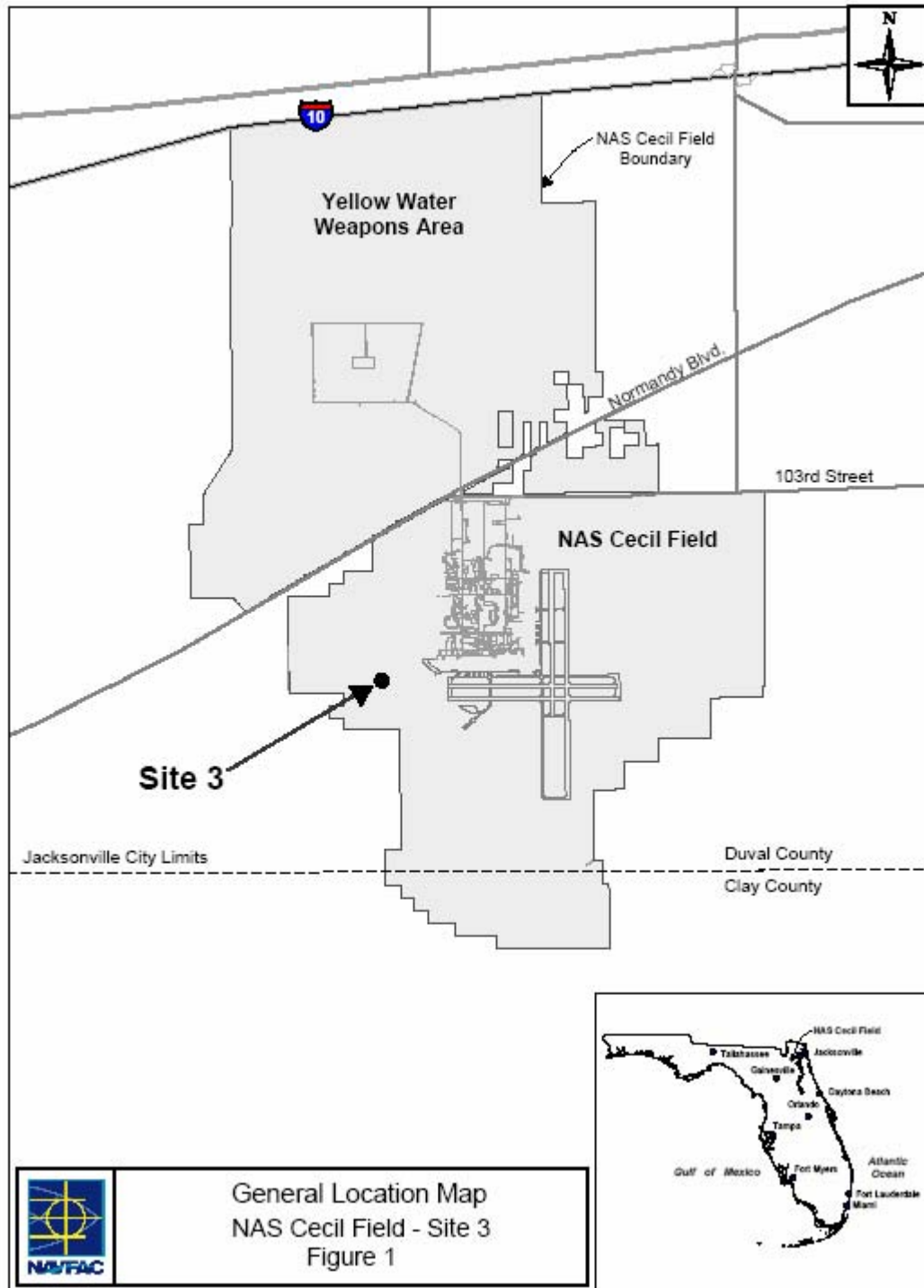
(Source: NAVFAC report, 2006)

1.3   Selection of Site

Site 3 is a waste oil and disposal pit located at the NASCF in Jacksonville, Florida. Ground water contamination that exceeds risk-based criteria at the site includes both volatile organic compounds (VOC's) and semi-volatile organic compounds (SVOC's).   The VOC's include soluble compounds such as trichloroethene (TCE), which are a concern due to their potential for impacting the nearby creek prior to complete degradation. The less soluble SVOC's such as naphthalene are a concern due to their potential longevity in reaching cleanup criteria in the source area. The remedy selected for the site included Air Sparging followed by MNA and Institutional Controls. Air Sparging was conducted intermittently from 1999 to 2002. The site is currently in the monitoring phase of MNA.
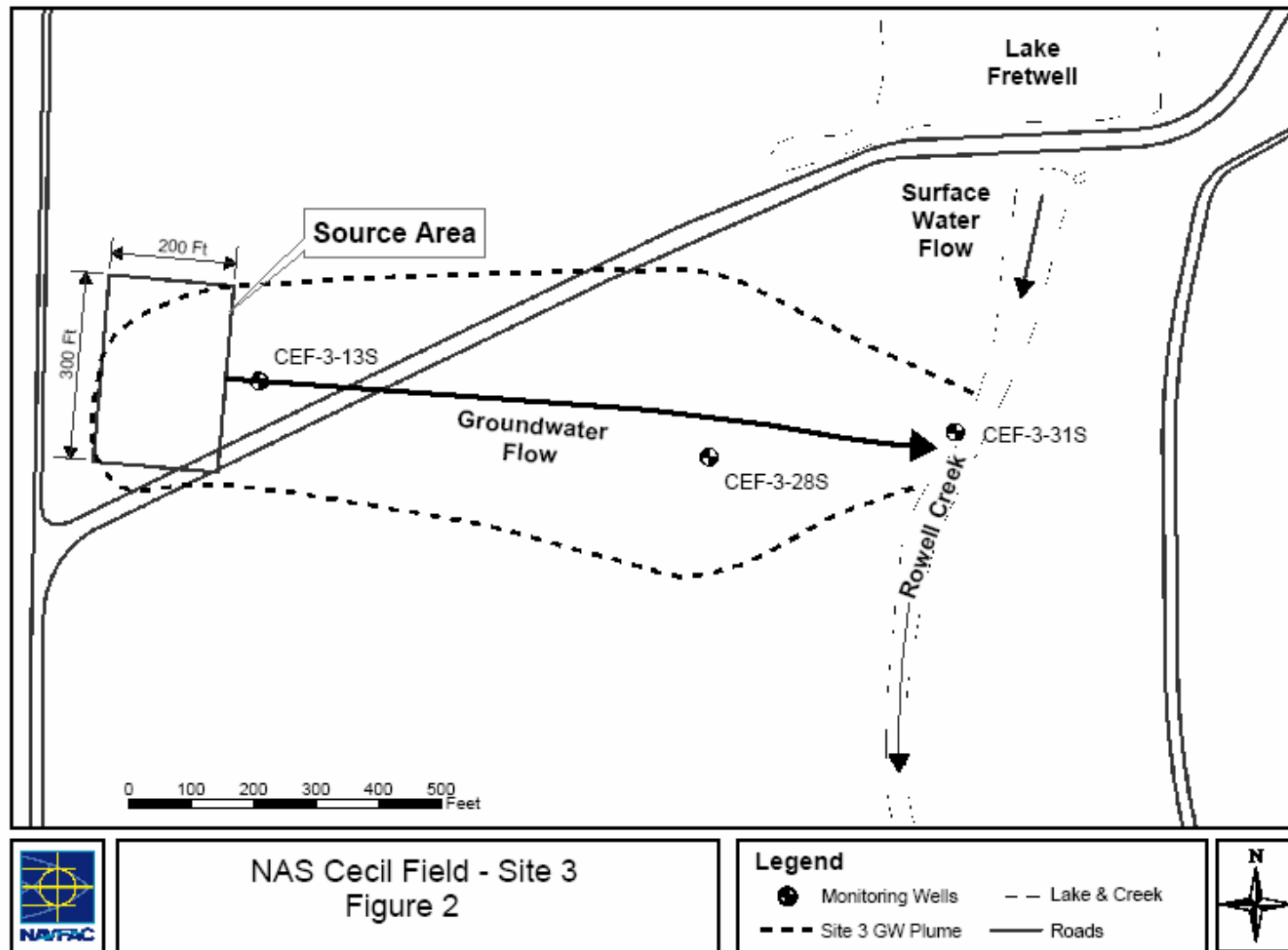
2.0   Site/Facility Characteristics

2.1   Hydrogeology

The topography of the site is relatively flat. From the disposal pit, the site gently slopes towards Rowell Creek (Figure 2). The impacted water bearing system in this area is the upper surficial aquifer, which has been characterized (ABB ES, 1996) as an unconfined system.   It is encountered at a depth of 3 to 5 feet below land surface (bls) near the location of the disposal pit and extends to a depth of approximately 50 feet bls where a confining layer is encountered. The average horizontal hydraulic gradient is approximately 0.005 foot per foot (ft/ft) at the waste disposal pit and increases to 0.035 (ft/ft) close to Rowell Creek. A portion of rainfall that falls on the site reaches ground water by infiltrating the soil and recharging the aquifer. This water flows in an east-southeasterly direction toward Rowell Creek where upward vertical gradients indicate it discharges.

The site lithology for the upper surficial aquifer from land surface to approximately 50 feet bls has been described (ABB-ES, 1996) as consisting of fine to medium-grained, poorly sorted quartz sand with some interbedded sandy clay, clayey sand and silty clay sand layers. A less permeable layer of sandy clay, clayey sand and clay of approximately 20 feet is located directly beneath this unit.

An aquifer test (Halford, 1996) conducted in the upper zone of the surficial aquifer near Site 3 provided estimates of hydraulic conductivity that ranged from 3 ft/d to 5 ft/d.   Assuming an effective porosity of 0.3, the seepage velocity is estimated to range from approximately 18 to 30 feet/year near the source area. This is expected to increase as the gradient becomes steeper near Rowell Creek. The rate of transport of contaminants however is less than the seepage velocity. This retarded rate of transport is due partly to chemical properties such as solubility and organic carbon distribution coefficient (K_{oc}) of the contaminants as well as the fraction of organic carbon (f_{oc}) in the aquifer.

Legend

- ⊕ Monitoring Wells
- – – Lake & Creek
- - - - Site 3 GW Plume
- —— Roads

NAS Cecil Field - Site 3
Figure 2

(Source: NAVFAC report, 2006)

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2.2   Source and Plume Description

Chemicals of concern in ground water identified during the RI, which include volatile organic compounds (VOC's), semi-volatile organic compounds (SVOC's) and a Polychlorinated Biphenyl (PCB) are listed in Table 1. In general the VOC's are more soluble and have lower K_{oc}'s than the SVOC's and PCB's. Therefore the rate of transport in ground water of VOC's is expected to be greater than the other compounds. The effect of a response or remedial action targeting the source area is expected to show up in the form of altered concentrations at the downgradient wells at times that are dependent on the retardation factor for each compound. Tables 2 through 4 list the selected VOC's (trichloroethene (TCE), cis-1,2 dichloroethene (DCE) and vinyl chloride(VC)) and SVOC's (naphthalene, 1,2 dichlorobenzene, 1,3 dichlorobenzene and 1,4 dichlorobenzene) that bracket the range of solubility's and K_{oc}'s of contaminants of concern at the site. The monitoring data for wells listed in these tables represent concentrations along the axis of the plume over time (Fig. 2). These monitoring events are expected to be representative of the ground water system prior to and after air sparging.

For VOC's in the source area (well CEF-3-13S, Table 2), TCE concentrations have dropped (1490 to 1170 ug/l) approximately 21 percent since the air sparging system was discontinued in late 2002. However, the degradation product, cis-1,2 DCE, is only 8 percent of its parent compound (TCE), whereas prior to sparging it was approximately 49 percent. TCE (1170 ug/l) remains well above the No Further Action (NFA) criteria of 3 ug/l.   The SVOC's (dichlorobenzenes and naphthalene) in the source area (well CEF-3-13S, Table 2) have increased from approximately 35 to 70 percent depending on the compound since the February 2003 sampling event. This may be a result of a longer timeframe necessary for these lower solubility compounds to come to equilibrium following sparging. The tendency of these compounds to sorb to the aquifer matrix and their lower rate of transport are expected to be potentially important factors in reaching NFA criteria for the site. These compounds are a factor of 6 to 10 times higher than the NFA criteria.

The precise dimensions of the disposal pit are uncertain. The lateral extent of the historical pit has been described differently in historical reports. One report (ABB, 1997) identifies the pit as having a diameter of approximately 50 to 100 feet, while another report indicates it consisted of a larger trench. Although the actual amount and composition of the waste disposed is not well known, the results from the RI identified the presence of VOC's and SVOC's consistent with waste oils and degreasing solvents. Soil and water samples collected during the RI were used to estimate the source area to be approximately 300 feet by 200 feet. Low levels of VOC's extend to a depth of at least 40 feet below land surface; however, the bulk of contamination appears to be in the upper 20 feet of the saturated zone.

Table 1. Contaminants of Concern and Range of Detection

Chemical of Concern	Range of Detection (ug/l)
1,1,1-Trichloroethane (TCA)	96 – 860
1,1-Dichloroethane (DCA)	1 – 590
1,1-Dichloroethene	2 – 350
1,2-DCE	9 – 1,900
Trichloroethene (TCE)	9 – 1900
Benzene	26
1,2-Dichlorobenzene (DCB)	350 – 9,800
1,3-Dichlorobenzene	9 – 240
1,4-Dichlorobenzene	49 – 1300
2,4-Dichlorophenol	5
2-Methylnaphthalene	0.8 – 200
4-Methylphenol	3 – 61
Naphthalene	0.6 – 450
Phenol	0.5 – 10
Bis-(2-ethylhexyl)phthalate	0.5 – 61
Aroclor	0.6 – 0.79

TABLE 2

SUMMARY OF SELECTED GROUND WATER MONITORING DATA
NAVAL AIR STATION CECIL FIELD
JACKSONVILLE, FLORIDA

PARAMETER	TARGET CLEANUP GOALS	MONITORING WELL CEF-3-13S				
		Operable Unit 8, Site 3				
		Mar-1994	Jun-1997	May 1999	Feb-2003	Jul-2005
VOLATILES (ug/l)						
Trichloroethene	3	1700	2300	2300	1490	1170
Cis-1,2-Dichloroethene	70	1900	970	1140	153	97.7
Vinyl Chloride	1	BD	BD	100U	20U	0.5U
SEMIVOLATILES (ug/l)						
1, 2-Dichlorobenzene	600	9800	6600	6140	2280	3870
1,3-Dichlorobenzene	210	240	200U	167	64.7	103
1,4-Dichlorobenzene	75	1300	1100	812	319	484
Naphthalene	14	450	NA	280	142	192

TABLE 3

SUMMARY OF SELECTED GROUND WATER MONITORING DATA
NAVAL AIR STATION CECIL FIELD
JACKSONVILLE, FLORIDA

PARAMETER	TARGET CLEANUP GOALS	MONITORING WELL CEF-3-28S				
		Operable Unit 8, Site 3				
		Mar-1994	Jun-1997	May 1999	Feb-2003	Jul-2005
VOLATILES (ug/l)						
Trichloroethene	3	480	360	381	366	244
Cis-1,2-Dichloroethene	70	120	130	1U	84	80.9
Vinyl Chloride	1	BD	BD	1U	1U	0.5U
SEMIVOLATILES (ug/l)						
1, 2-Dichlorobenzene	600	600	570	442	253	185
1,3-Dichlorobenzene	210	17	50U	12.2	7.8	5.4
1,4-Dichlorobenzene	75	83	140	59.1	34.9	25.2
Naphthalene	14	77	NA	65.9	40.9	37.8

TABLE 4

SUMMARY OF SELECTED GROUND WATER MONITORING DATA
NAVAL AIR STATION CECIL FIELD
JACKSONVILLE, FLORIDA

PARAMETER	TARGET CLEANUP GOALS	MONITORING WELL CEF-3-31S				
		Operable Unit 8, Site 3				
		Mar-1994	Jun-1997	May 1999	Feb-2003	Jul-2005
VOLATILES (ug/l)						
Trichloroethene	3	48	BD	1U	1U	0.6
Cis-1,2-Dichloroethene	70	9	120	170	221	151
Vinyl Chloride	1	BD	BD	1.1	1.8	5.7
SEMIVOLATILES (ug/l)						
1, 2-Dichlorobenzene	600	10U	10U	5U	6.7	10.8
1,3-Dichlorobenzene	210	10U	10U	5U	1.1U	0.94U
1,4-Dichlorobenzene	75	10U	10U	5U	1.1U	0.94U
Naphthalene	14	10U	NA	5U	1.1U	0.94U

2.3 Past and Current Remediation Strategies

A Record of Decision (ROD) for ground water contamination at Site 3 was signed in 1998. The regulatory framework used to develop the ROD included the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the National Contingency Plan (NCP) and the Florida Department of Environmental Protection (FDEP), Florida Administrative Code (FAC) 62-550 and public comments. The remedy selected to address contaminants in ground water included a combination of alternatives: In-situ Air Stripping of Source Area Ground water by Air Sparging, Monitored Natural Attenuation (MNA) of Downgradient Ground water and implementation of Institutional Controls using deed restrictions to limit the use of contaminated ground water. Air Sparging in the source area began in 1999 and was used intermittently through 2002 when it was last operated. MNA is an ongoing part of the remedy and ground water samples are collected semi-annually to evaluate its performance.

2.4 Groundwater Flow and Transport Modeling – Previous work

An estimate of the time to reach the cleanup goal for TCE in the source area was developed in the Remedial Design (TTNUS, 1998). This estimate was 16.5 years based on the assumption that a reduction in the source concentrations of TCE to 1255 ug/l would allow residual concentrations to naturally attenuate during that period. Using this approach, TCE served as a surrogate measure of TOR for other contaminants at the site.

3.0 Demonstration Approach

3.1 Modeling Objective

Site 3 offer an opportunity to evaluate NAS for simulating concentration versus time for contaminants derived from a mixed NAPL source. NAS was used to simulate observed concentration data from a source zone monitoring well for TCE, DCE, naphthalene, and chlorobenzenes.

3.2 Input Parameters

3.2.1 Hydrogeologic Data

The data inputs used in NAS are provided in Table 5. Selected VOC's and SVOC's from the list of Chemicals of Concern were used in the simulation to estimate the TOR at the site for which NFA would be necessary. Until NFA goals are met, long term monitoring, reporting and institutional controls are required. NFA goals are met when the cleanup goals for ground water discussed above have been met. The compounds selected for simulation were intended to bracket the range of properties that affect ground water transport such as solubility and K_{oc}. For VOC's, the compounds TCE, cis-1,2 DCE and VC were used. These compounds exhibit higher solubility's and lower K_{oc}'s. Naphthalene and three isomers of dichlorobenzene were the SVOC's used in the simulation. The SVOC's have lower solubility's and higher K_{oc}'s. Values

used in this simulation were those derived from samples collected in saturated sediments versus unsaturated soil. Table 6 lists the values used in this simulation. Uncertainties about the physiochemical properties of hydrophobic compounds such as the SVOC's can affect the outcome of fate and transport models such as NAS. This problem has been recognized (Renner, 2002) as a deficiency in many of the existing chemical databases and should be considered when interpreting the solutions for TOR.

Table 5. Hydrologic parameters used in NAS simulations

	Maximum	Average	Minimum
Hydr. Conductivity [ft/d]	43	40	38
Hydraulic Gradient [ft/ft]	0.003	0.002	0.001
Total Porosity [-]		0.3	
Effective Porosity [-]		0.3	
Groundwater Vel. [ft/d]	0.43	0.267	0.127

Contaminant Source Specifications

Source Component	Conc Profile	NAPL Constituent
Total CBs	TRUE	TRUE
13DCB	TRUE	TRUE
12DCB	TRUE	TRUE
14DCB	TRUE	TRUE
CB	TRUE	TRUE
Benzene	TRUE	TRUE

Dispersion Parameters

Estimated Plume Length [ft]	743.4
Longitudinal Dispersivity [ft]	21.54
Dispersivity Ratio [-]	20
Transverse Dispersivity [ft]	1.08

Sorption Parameters
Fraction Org. Carbon [-]

Maximum	0.001
Average	0.001
Minimum	0.001

	NAPL Source
NAPL Source Length [ft]	50
NAPL Source Width [ft]	50
Contaminated Aquifer Thickne	3

Table 6. Chemical and Physical Properties of Solutes

Analyte	Soil Sorption Coefficient, (Koc)	Aqueous Solubility (mg/l @ 25 C)	Molecular Weight
Trichloroethene (TCE)	126	1100	131.38
cis –1,2 Dichloroethene (cDCE)	65	3500	96.94
Vinyl Chloride (VC)	57	2763	62.50
Naphthalene (N)	871	31.7	128.20
1,2 Dichlorobenzene (1,2 DCB)	500	156	147.01
1,3 Dichlorobenzene (1,3 DCB)	500	125	147.01
1,4 Dichlorobenzene (1,4 DCB)	500	80	147.01

Sources: USACE (2002), IPCS 2004, Superfund Chemical Data Matrix (EPA, 1996), Davis 1997, Perry and others 1994, Chiou and Kile (USGS, 2000)

3.2.2 Source Characteristics

The source area was based on estimates of the locations where contaminants were identified during the remedial investigation. The bulk of the mass appears to be confined to a rectangular block that is as large as 300 feet wide by 200 feet long by 20 feet in depth. Previous estimates (TTNUS, 1998) of the mass of dissolved TCE in the source area approach 75 pounds. The total mass of CVOC's, SVOC's as well as other constituents sorbed to or diffused into the aquifer matrix are likely one to two orders of magnitude greater than the dissolved phase. For this simulation a range of values for total contaminant mass were evaluated from 1000 to 10,000 kg. The waste fuels and solvents were assumed to be disposed as non-aqueous phase liquids (NAPL). The fraction of each individual compound in the NAPL was estimated largely on trial and error to match the historical trends. The estimated mass fraction for each compound in the NAPL is listed in Table 5. Estimates of source area mass are those assumed to exist in 1975 when disposal operations ceased.

4.0   Performance Assessment

Estimates of TND were evaluated for a range of values for contaminant mass and transport velocities. The first set of outputs (Graphs 1 – 6) relates historical concentration data near the source area (CEF-3-13S) to a range of mass estimates at the average seepage velocity (18 ft/yr). The last set of outputs (Graphs 7 – 12) reflects the sensitivity to the range of seepage velocities

(11 and 33 ft/yr for the minimum and maximum velocities) of the contaminants relative to historical data. Based on Graphs 1 –6, the VOC's appear to be most sensitive to estimates of mass during the early stages of NAPL dissolution. During these periods the more soluble compounds elute early and a more pronounced peak is observed in the plume concentrations. The predicted late term behavior of the plume for each estimate of mass begins to reach similar values around the year 2025. For TCE, the average mass (5000 kg) estimate appears to track the observed data (Graph 1) near the base of the predicted peak of contaminant concentrations. The degradation product, cis-1,2 DCE, follows the shape of the curve (Graph 2) initially but the last two observed data points are noticeably lower than the predicted values. These last two data points represent the source area after sparging. This behavior is consistent with the potentially adverse impact of the sparging system on dechlorination activity observed at the site.

The SVOC's and particularly naphthalene reflect a more gradual decline in contaminant concentrations over time than the VOC's. The early parts of the graphs (3 through 6) are very similar regardless of the mass estimate used. This behavior is expected as these lower soluble compounds are expected to more slowly dissolve into the water column. However the tail of the graphs become more distinct and the estimates of contaminant concentration diverge as the length of time increases. The observed data has a similar shape relative to the predicted trends in concentrations however the simulations appear to predict an earlier release of the solutes than what is observed. One possible explanation for this behavior includes deviations caused by less accurate estimates of the chemical properties associated with the SVOC's.

Since the observed data more closely follows the average estimate (5000 kg) of mass for both VOC's and SVOC's, this value was used to estimate the TOR. In order to capture the earliest and latest estimates of TOR (Table 7) the range of transport velocities was evaluated (Graphs 7 – 12). The potential range of transport velocities predicts a wide range of TOR estimates that encompass the observed time series data. This is partially related to the f_{oc} values that varied by an order of magnitude.

The TOR for MNA to achieve NFA criteria is listed in Table 8. These timeframes represent periods starting in 1975 when disposal operations ceased. Model simulation and procedures were discussed in Section 3.2 and provide the basis of these estimates. Previous estimates of TOR assumed TCE would serve as a surrogate compound for all site contaminants. This probably underestimates the TOR by at least a factor of two based on a comparison of the lowest estimate of TOR (Table 8) by compound relative to naphthalene. As discussed above, chemical properties associated with SVOC's may result in longer estimates of TOR relative to VOC's. This is particularly true for naphthalene, which has a low target cleanup goal (14 ug/l) as well as the lowest solubility and highest K_{oc} of the compounds evaluated. Using naphthalene as a site limiting contaminant of TOR suggests the site will not meet NFA criteria until a time in excess of 100 years (version 2.2.1 of NAS has a maximum simulated TOR of 100 years) beginning in 1975. If this estimate is off by a factor of two, it will take in excess of 50 years to reach 14 ug/l via MNA or at least 19 additional years from the year 2006. Using the average estimate of mass in the source area, the TOR for TCE is approximately 74 years from 1975.
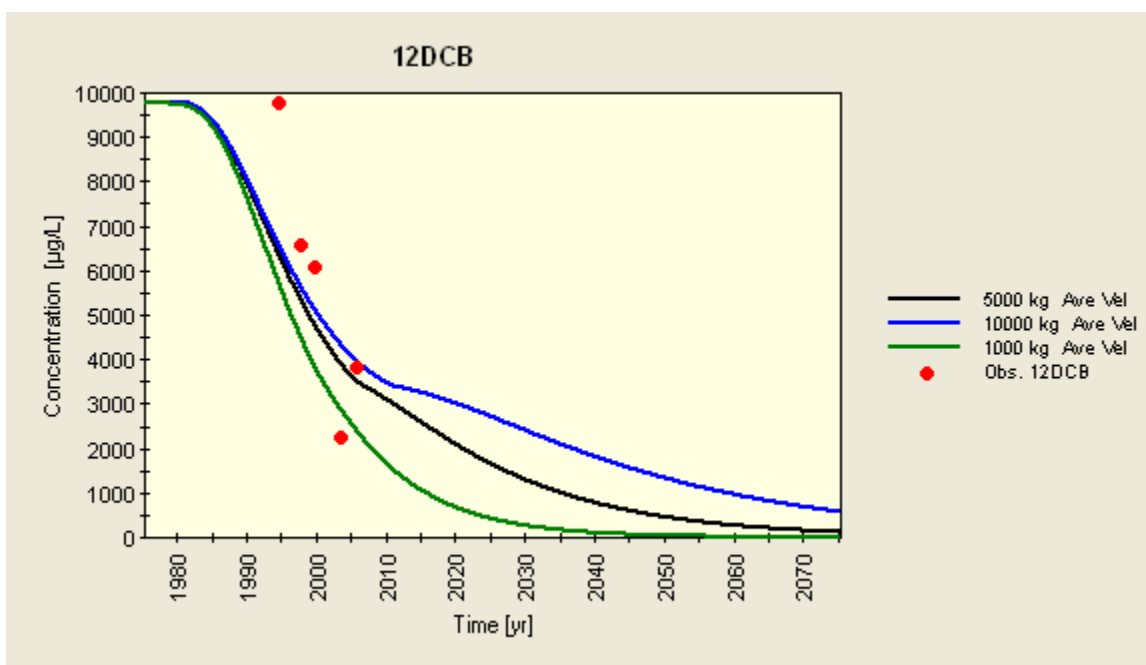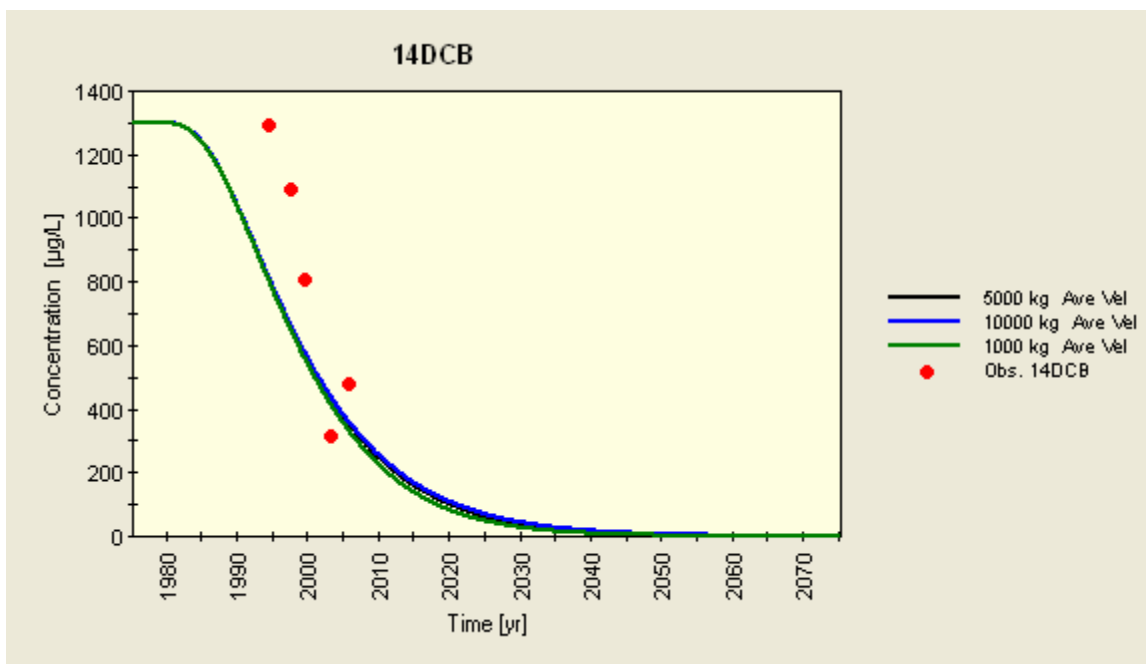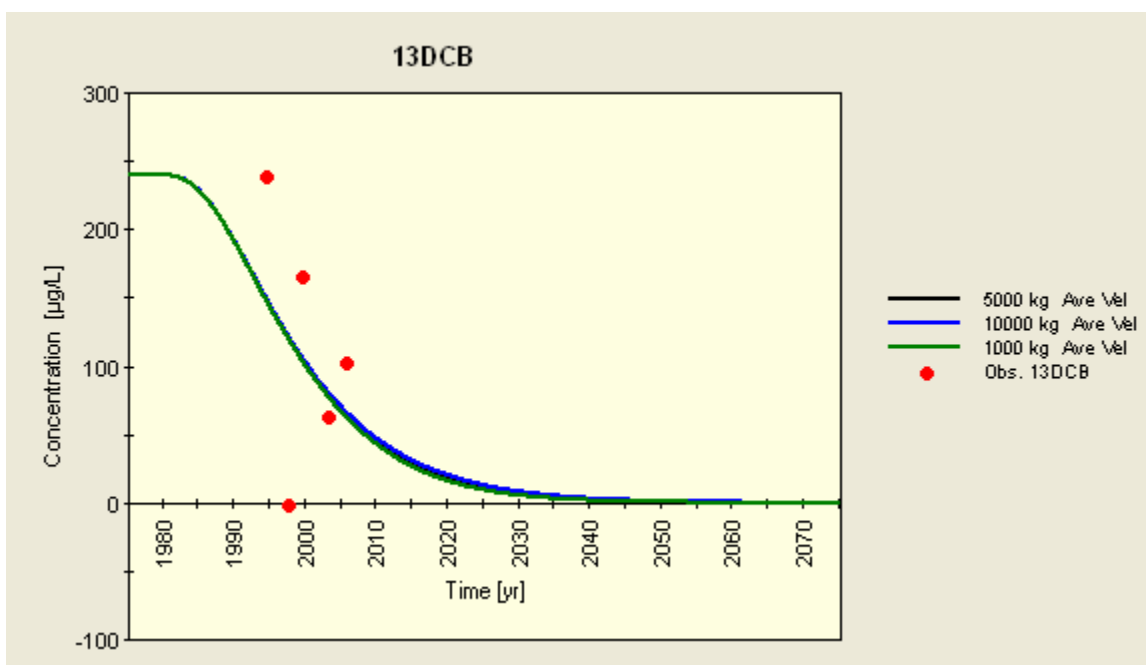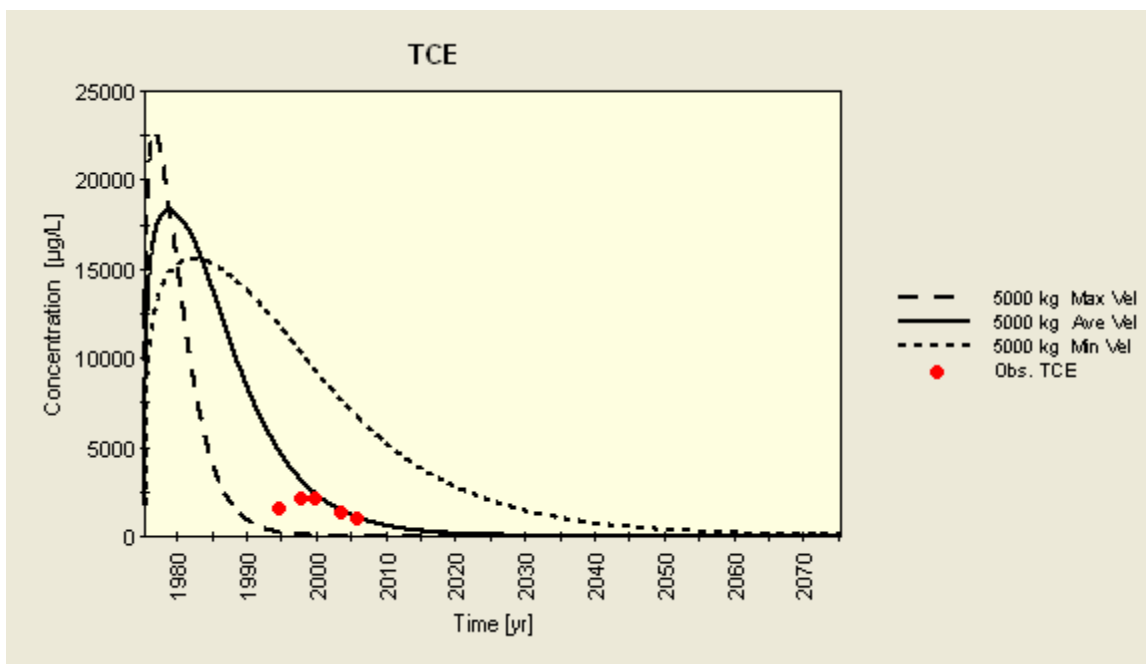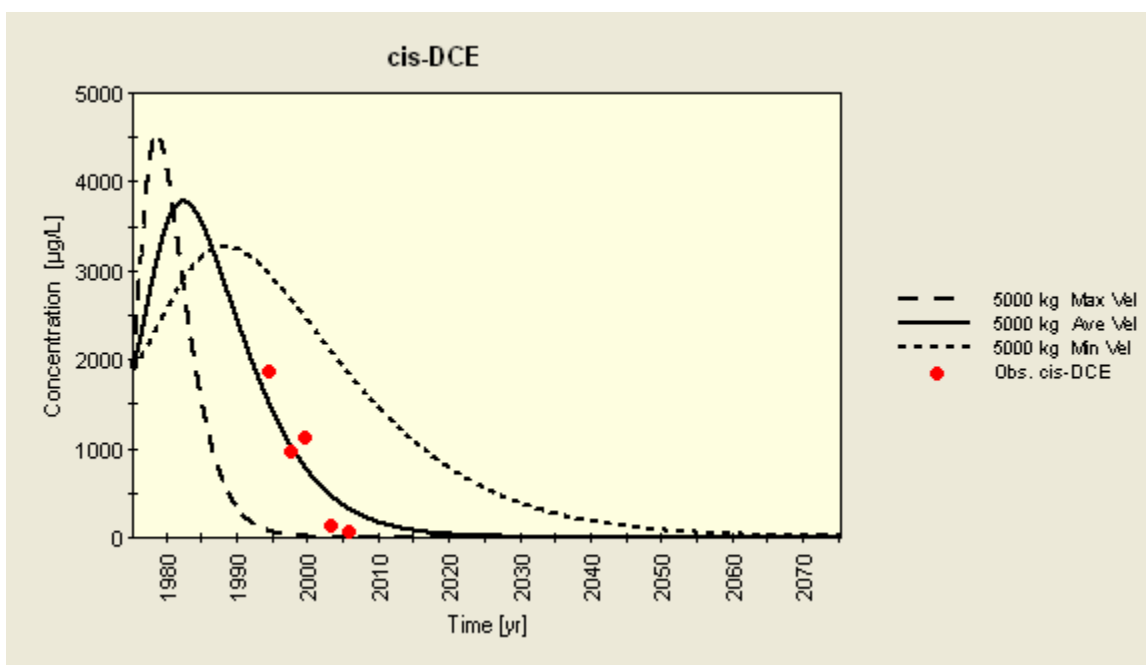
Graph 1

Graph 2.

F-15
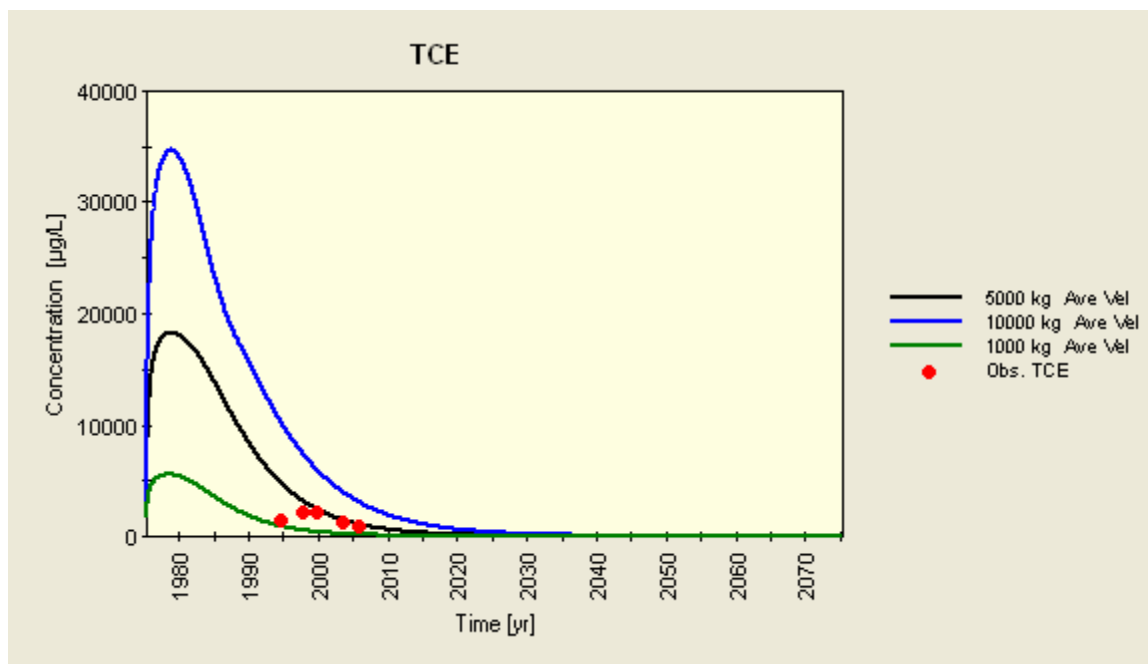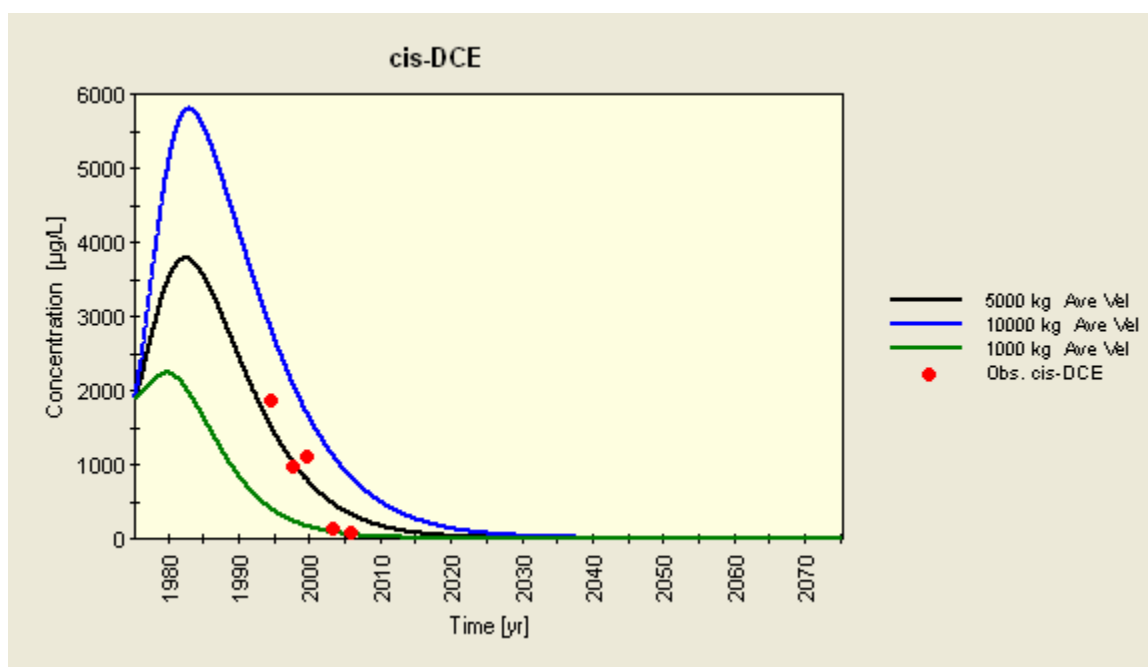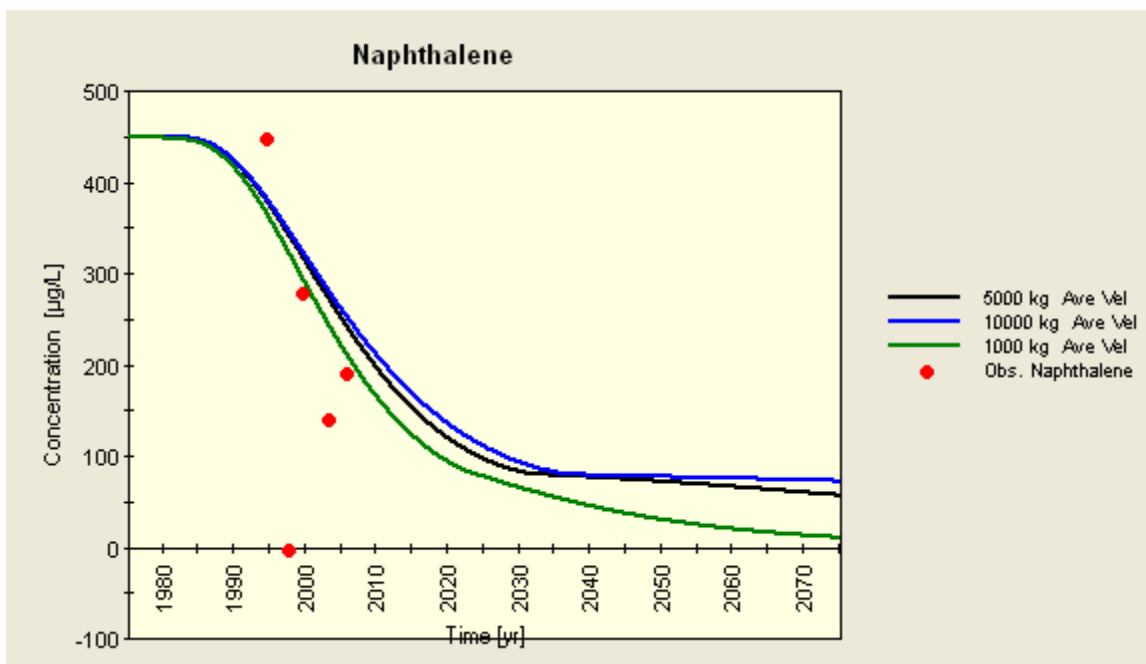
Graph 3

Graph 4
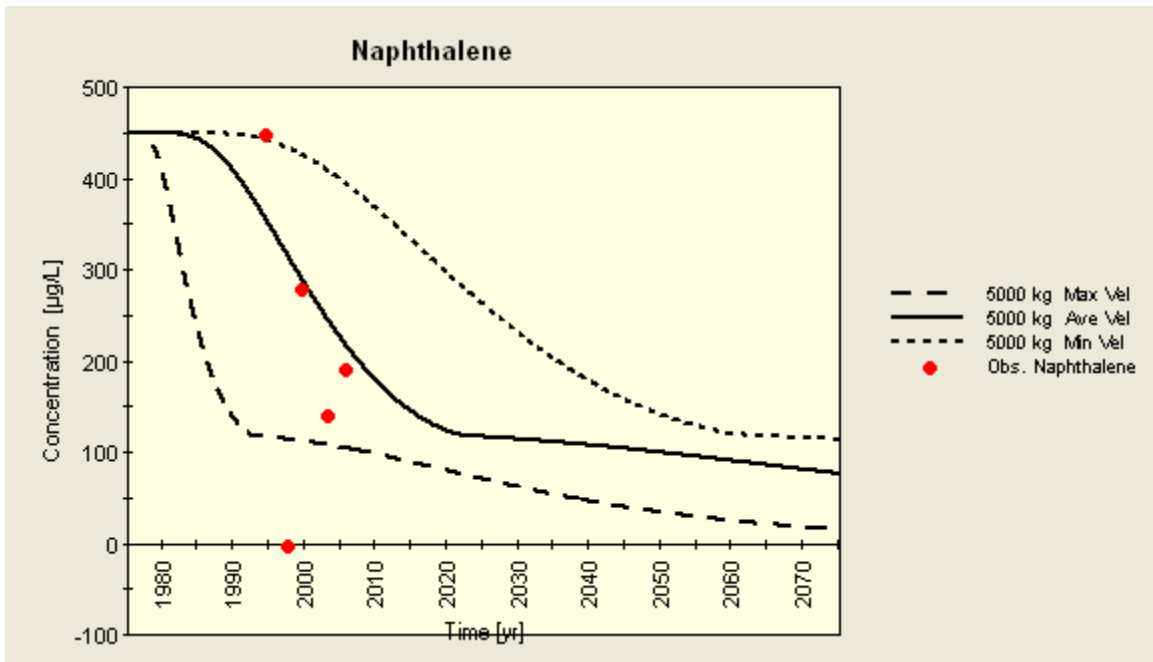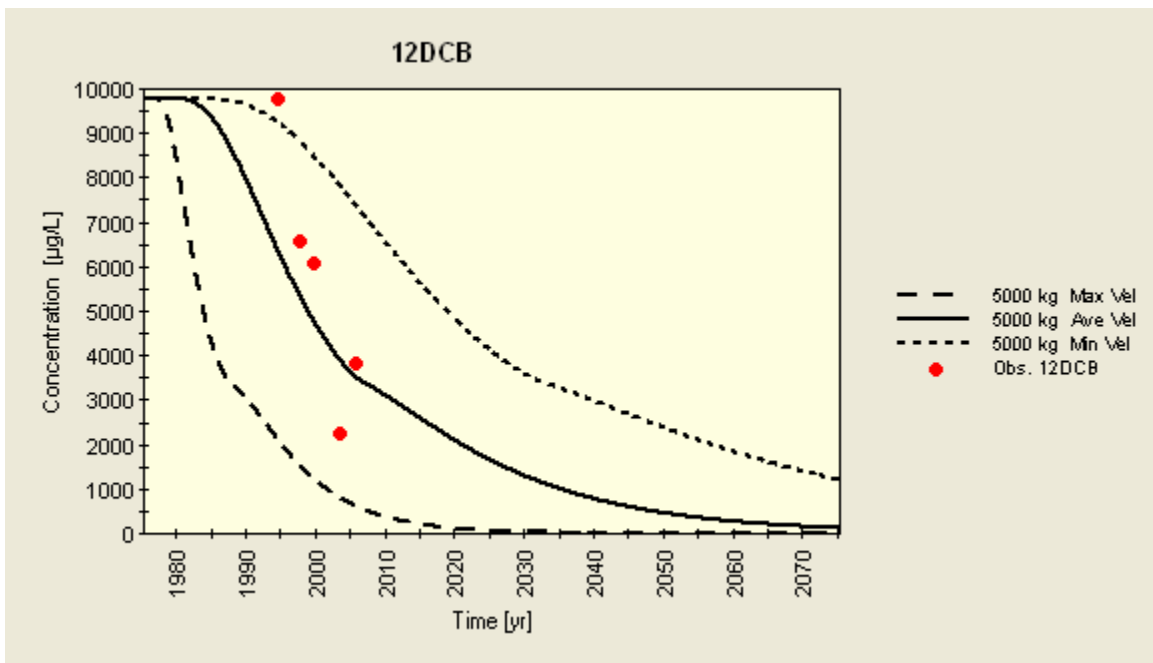
Graph 5

Graph 6

Graph 7
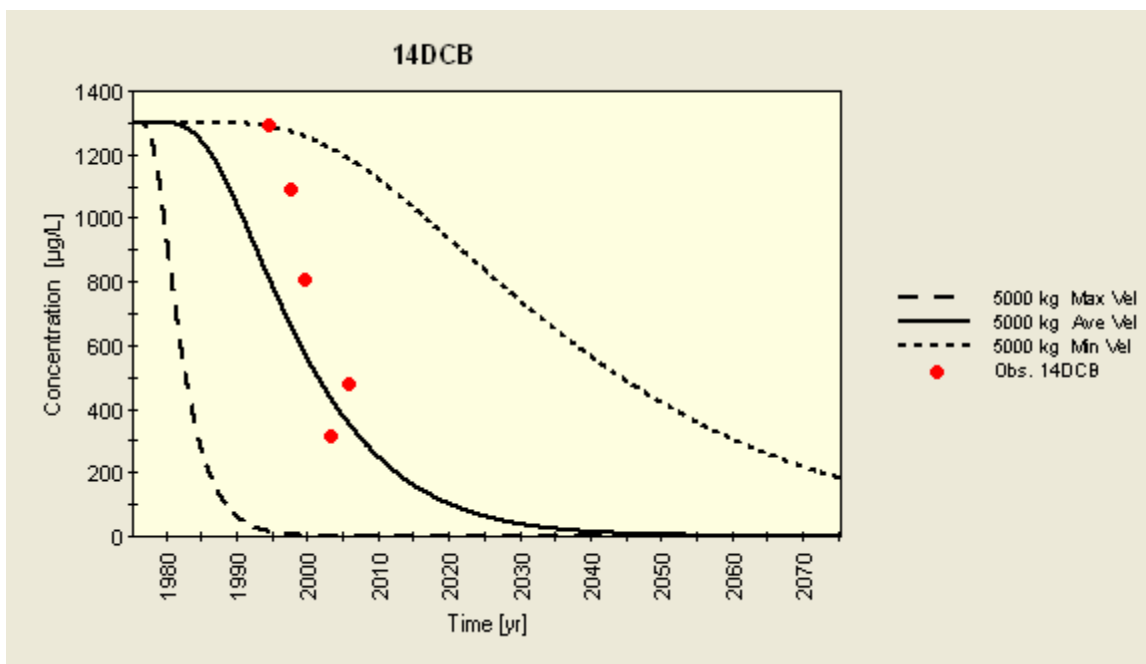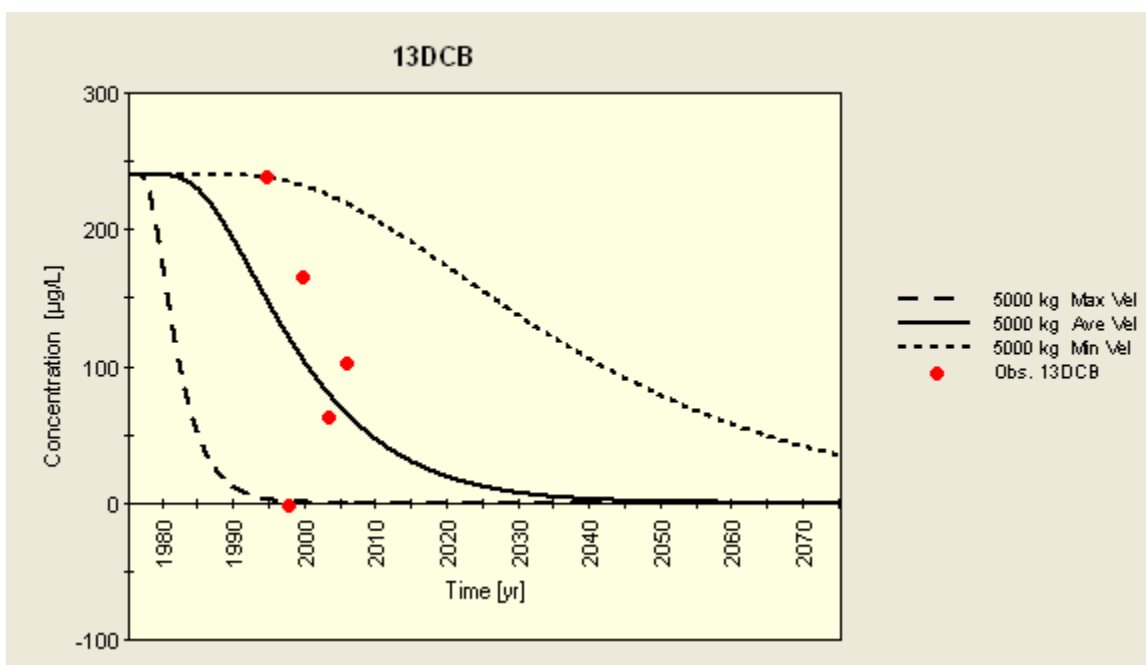

Graph 8

F-18

Graph 9

Graph 10

Graph 11

Graph 12

F-20

Table 7. Time of Remediation Associated with High and Low Transport Velocities

		SCC [µg/L]	Mass [kg]	TOR MNA
Max Time of Analysis [yr]	100			
TCE	3.0		10,000	43.4 - 100+
			5,000	34.2 - 100+
			1,000	24.7 - 100+
cis-DCE	70.0		10,000	25.6 - 95.7
			5,000	20.7 - 78.3
			1,000	14.7 - 57.2
Vinyl Chl.	1.0		10,000	40.8 - 100+
			5,000	34.6 - 100+
			1,000	27.9 - 100+
Naphthalene	14.0		10,000	100+ - 100+
			5,000	84.6 - 100+
			1,000	29.9 - 100+
12DCB	600.0		10,000	51.3 - 100+
			5,000	32.2 - 100+
			1,000	16.4 - 100+
14DCB	75.0		10,000	14.4 - 100+
			5,000	14.4 - 100+
			1,000	13.8 - 100+
13DCB	210.0		10,000	3.7 - 34.0
			5,000	3.7 - 34.0
			1,000	3.7 - 33.9

TOR has been shown to be sensitive to ground water velocities (Chapelle, et. al. 2003) and one of the primary differences between the previous TOR estimate (TTNUS, 1998) and these simulations is the data used to estimate the seepage velocity. Although both simulations used an estimate of 3 ft/day for hydraulic conductivity, the values for hydraulic gradient and effective porosity were significantly different. The 1998 estimate averaged the hydraulic gradient from the source area and the downgradient section of the plume near the creek for a value of 0.016 ft/ft. This is over three times the value (0.005 ft/ft) at the source area, which was used in this simulation. In addition, the effective porosity used in the 1998 estimate was 0.2 versus 0.3 in these simulations. The differences in hydraulic conductivity and effective porosity results in a seepage velocity of approximately 18 ft/yr for the source area in this study versus 88 ft/yr in the 1998 estimate. The 1998 estimate reflects conditions that may be similar to site wide average conditions with respect to the hydraulic gradient but potentially over predicts the velocity at the source area and thus a critical value in estimating TOR at that location. An estimate of the TOR associated with the effective porosity (0.2) used in the 1998 estimate was calculated to evaluate its magnitude relative to the current estimate. The results of this estimate (Table 9) of TOR

remain in excess of 100 years for naphthalene but are reduced to 61 years for TCE. This reinforces the importance naphthalene as a controlling factor in estimates of TOR at site 3.

Table 8. Time of Remediation Associated with Average Transport Velocities

Max Time of Analysis [yr]	100		
	SCC	**Mass**	**TOR**
	[μg/L]	**[kg]**	**MNA**
TCE	3.0	10,000	**92.5**
		5,000	**74.8**
		1,000	**55.8**
cis-DCE	70.0	10,000	**53.1**
		5,000	**43.4**
		1,000	**31.0**
Vinyl Chl.	1.0	10,000	**84.8**
		5,000	**72.5**
		1,000	**58.7**
Naphthalene	14.0	10,000	**100+**
		5,000	**100+**
		1,000	**92.8+**
12DCB	600.0	10,000	**100+**
		5,000	**76.9**
		1,000	**48.0**
14DCB	75.0	10,000	**49.6**
		5,000	**48.6**
		1,000	**46.2**
13DCB	210.0	10,000	**12.8**
		5,000	**12.8**
		1,000	**12.8**

Uncertainties associated with these estimates have been previously discussed in this report but are worth briefly summarizing. The ground water system is heterogeneous and values used are either estimates of values for the site and/or values assumed to be applicable to this system. Estimates of the average hydraulic conductivity were determined by an aquifer test however regions of finer grained or coarser grained aquifer sediment may result in lower or higher rates of flow. The rates of ground water flow and geometry of the source area affect the time of NAPL dissolution. Higher rates of flow and smaller dimensions of the source geometry may result in lower times of remediation. There were no known measured values for f_{oc} at the time of this study therefore; estimates from published literature were used as a guide. To address this element, TOR was estimated with a range of f_{oc} values that varied an order of magnitude. The higher and lower values of f_{oc} were used in the calculations of TOR as part of the estimates of maximum and minimum transport velocities (Graphs 1 – 6). Greater amounts of f_{oc} will result in greater retardation of the solutes, particularly the SVOC's that have higher K_{oc}'s. The transport

velocities reflect retardation of groundwater transport for each solute relative to the seepage velocity by a compound specific retardation factor (Appendix C). The horizontal and vertical distribution of contamination is generally known but there is significant variation over the bounds of the source area. Accordingly, the amount of contaminant mass at the site is unknown, however, estimates of the dissolved mass in ground water for TCE was used to estimate the amount of potential mass in the aquifer matrix. Values of mass that ranged an order of magnitude were used to estimate the potential high and low TOR. A wide range of values for K_{oc} and solubility for some of the SVOC's appear in published literature (Chiou and Kile, 2000), which suggests a larger range of uncertainty than for the VOC's. Doubts about the quality of physiochemical data for hydrophobic compounds such as the SVOC's has been recognized elsewhere (Renner, 2002) which may affect the outcome of fate and transport models such as NAS.

Table 9. Time of Remediation Associated with an Effective Porosity of 0.2

Max Time of Analysis [yr]		100	
	SCC [µg/L]	Mass [kg]	TOR MNA
TCE	3.0	5,000	**61.1**
cis-DCE	70.0	5,000	**34.8**
Vinyl Chl.	1.0	5,000	**56.6**
Naphthalene	14.0	5,000	**100+**
12DCB	600.0	5,000	**70.5**
14DCB	75.0	5,000	**42.0**
13DCB	210.0	5,000	**11.0**

5.0   References

ABB-ES, 1996. Remedial Investigation, Operable Unit 8, Site 3, Naval Air Station Cecil Field, Jacksonville, Florida. Prepared for Southern Division, Naval Facilities Engineering Command.

ABB-ES, 1997. Feasibility Study, Operable Unit 8, site 3, Naval Air Station Cecil Field, Jacksonville, Florida. Prepared for Southern Division, Naval Facilities Engineering Command.

Bradley, P.M., and F.H. Chapelle. 1996. Anaerobic mineralization of vinyl chloride in Fe (III)-reducing aquifer sediments. Envrion. Sci. Technolo. 30:2084-2086.

Bradlley, P.M., F.H. Chapelle, and D.R. Lovley. 1998. Humic acids as electron acceptors for anaerobic microbial oxidation of vinyl chloride and dichloroethene. App. Environ. Microbiol. 64:3102-3105.

Chapelle, F.H., Widdowson, M.A., Brauner, J.S., Mendez, E., and Casey, C.C.. 2003. Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation. United States Geological Survey Water Resources Investigations Report 03-4057.

Chiou, C.T. and Kile, D.E., 2000. Contaminant Sorption by Soils and Bed Sediment –Is there a Difference? USGS Fact Sheet 087-00.

Envirodyne Engineers, 1985, Initial Assessment Study of Naval Air Station Cecil Field, Jacksonville, Florida: prepared for Naval Energy and Environmental Support Activity, Port Hueneme, California, NEESA 13-073, July.

Halford, K.J. 1996. Ground-Water Flow in the Surficial Aquifer System and Potential Movement of Contaminants from Selected Waste-Disposal Sites at Cecil Field Naval Air Station, Jacksonville, Florida. United States Geological Survey. Administrative Release.

International Programme on Chemical Safety (IPCS), 2004, CHLOROBENZENES OTHER THAN HEXACHLOROBENZENE: ENVIRONMENTAL ASPECTS. Concise International Chemical Assessment Document 60.

NAVFAC (Naval Facilities Engineering Command), 2001, *Guidance for Optimizing Remedial Action Operation (RAO) Interim Final*, SR-2101-ENV, April.

Renner, Rebecca, 2002, The K_{OW} Controversy. Environmental Science and Technology, v. 36, no. 21, pp. 411A-413A

Spitz, K. and Moreno, J. 1996. A Practical Guide to Ground water and Solute Transport Modeling. Wiley InterScience. Appendix D, Table D-6.

TTNUS, 1998. Groundwater Remedial Design Operable Unit 8, Site 3 for NAS Cecil Field, Jacksonville, Florida. Prepared for Southern Division, Naval Facilities Engineering Command. October.

USACE (U. S. Army Corps of Engineers), 2002. Engineering Manual EM1110-1-4001. Appendix B, Properties of Common Organic Pollutants. June.

Appendix G: NAS Pensacola, FL – WWTP

NAS Pensacola, FL – Waste-Water Treatment Plant (WWTP)

1.0   Chlorobenzene Test Site

1.1   History of Operations at the Site

The WWTP has been used to process wastewater since 1941, when the sewage treatment facility was first installed. During the 1950's and 60's, the WWTP received industrial waste from paint and electroplating operations. Much of this waste was processed concurrently with sewage waste. In 1971, the WWTP was upgraded to separate the treatment of industrial and domestic wastes. Wastewater treated at this site contained organic solvents (including chlorinated ethenes, benzene, and chlorobenzenes), phenols, chromium electroplating wastes (including cyanide and other heavy metals), and wastes from a chemical conversion coating process for aluminum. Drying beds were used to dewater the sludges generated by the waste-treatment processes. These abandoned drying beds were the source of environmental contamination that was addressed under RCRA.

1.2   Present Operation of the Site

The WWTP continues to be used to treat domestic sewage generated at NAS Pensacola. In addition, and due to the demonstrated success of oxygen addition in remediation the source area, an air-sparging system was installed to inject air into the chlorobenzene hotspot in the spring of 2005. This system will be operated for a limited period of time to decrease chlorobenzene contamination in the hot spot.

1.3   Selection of Site

Plume C-C' at the WWTP, NAS Pensacola, was selected to test the NAS software because it is an example of a chlorobenzene-contaminated site, because the data sets include monitoring of a source area-reduction action (the ORC® the injection of 2001), and because the NAPL source area has been delineated so that NAPL dissolution can be considered.

2.0   Site/Facility Characteristics

2.1   Hydrogeology

The WWTP is underlain by marine and fluvial terrace sediments deposits of Quaternary age. Sediments exposed at land surface and extending to a depth of about 40 feet are predominantly fine to medium sands that form a shallow water-table aquifer. This water-table aquifer is underlain by lower-permeability silts and clays of marine origin that act as a confining bed. This confining bed is underlain by permeable sands and gravel that form a confined aquifer system. This confined aquifer is known locally as the "main producing zone" and has been used for water

supply. At the WWTP, the confined main producing zone has higher water levels than the overlying water-table aquifer. Thus, the site is characterized by an upward hydraulic gradient. The combination of the confining bed and the upward hydrologic gradient prevents downward movement of ground water at this site (Ensafe/Allen and Hoshall, 1995). Because of this, most of the contaminants are present in the water-table aquifer between a depth of 20 to 40 feet below land surface. Pensacola Bay, located immediately adjacent to the WWTP, serves as the regional discharge area for both the shallow water-table aquifer and the underlying main producing zone.

2.2   Hydrogeology

The chlorinated ethene plume present at the WWTP is delineated by section A-A' (Fig. 1), and the chlorinated benzene plume is delineated by section B-B'. In situ oxidation of chlorinated ethenes at the source area of the A-A' plume was applied in December 1998 and May 1999, in the vicinity of well USGS-5 AND IMW-66 (Geo-Cleans, 1999). The "hotspot" of benzene and chlorinated benzene is located near SMW-8, and is delineated by section C-C' (Fig. 2). The locations of the ORC® injections designed to treat this hotspot, and the locations of monitoring wells designed to assess treatment effectiveness are also shown in Figure 2.

2.2   Source and Plume Description

Studies by the U.S. Geological Survey beginning in 1996 (U.S. Geological Survey, 1999) indicated that conditions were favorable for natural attenuation processes to treat chlorinated ethene-contaminated ground water. Specifically, it was shown that chlorinated ethenes were rapidly transformed to non-toxic byproducts (carbon dioxide, chloride, and ethane) prior to discharging into Pensacola Bay. Chlorinated benzenes were more recalcitrant under the ambient anoxic conditions of ground water, but were removed at the freshwater/saltwater mixing zone of the aquifer prior to reaching Pensacola Bay. The observed chlorobenzene removal appears to reflect the combined effects of mixing at the freshwater/saltwater interface near Pensacola Bay and biodegradation processes. In response to the results of these studies, operation of the ground-water pumping system was discontinued and additional environmental monitoring was instituted to verify the continued effectiveness of natural attenuation processes at the site. Ground water has been monitored on a quarterly or semi-annual basis since 1987. In addition, the natural attenuation of chlorinated ethenes and benzenes have been monitored along flowpath A-A' and B-B' since 1996 (Fig. 1), and along flowpath C-C' since 1999 (Fig. 2).
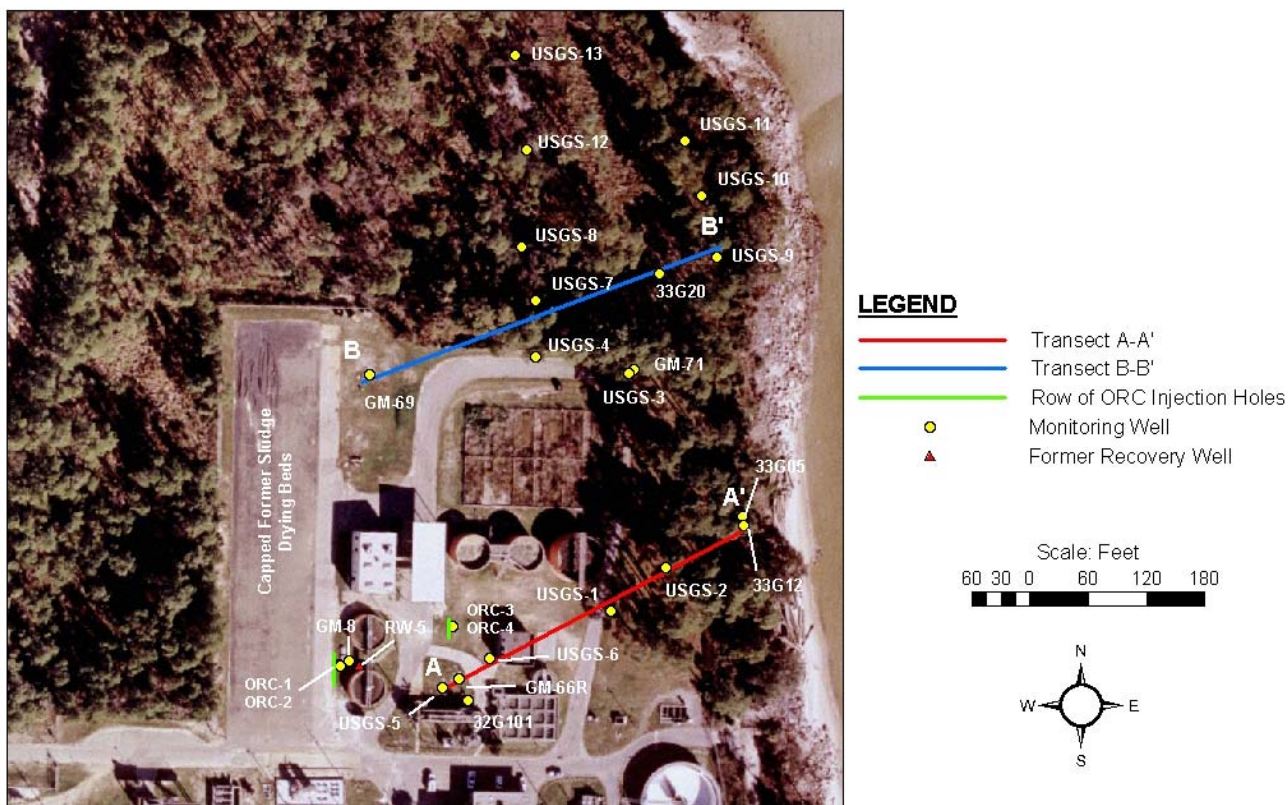
Figure 1. Location of Monitoring wells used to delineate flowpaths A-A' and B-B', and the location of ORC injection lines. (Source: U.S. Geological Survey. 1999. Natural Attenuation of Chlorinated Ethenes and Chlorinated Benzenes, Wastewater Treatment Plant, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina).

The size of the chlorobenzene source impacting SMW-8 was determined by geoprobing a series of holes surrounding SMW-8, sampling the ground water at three-foot vertical increments, and analyzing the water using a field gas chromatograph (U.S. Geological Survey, 2000). Based on the results of this study, Oxygen Release Compound (ORC®) was injected along two lines on March 24, 2001, to enhance biodegradation of chlorobenzene. The line nearest the capped drying beds consisted of 12 holes spaced between four and one feet apart. The downgradient line consisted of six holes spaced four feet apart. The locations of the ORC® injection holes and the monitoring wells installed to monitor the effectiveness of this remediation are shown in Figure 2.

The ORC® injections were performed using direct-push technology. For each ORC® hole, the tool was pushed to a depth of 40 feet and the drill rods lifted about six inches to separate the aluminum drill tip. This opened the drill rods so that ORC® could be pumped into the open hole left by the rods. Forty lbs of ORC® mixed with 10 gallons of tap water was pumped into each hole. The ORC® was distributed as uniformly as possible between depths of 40 and 4 feet below land surface as the drilling rods were removed from each hole.
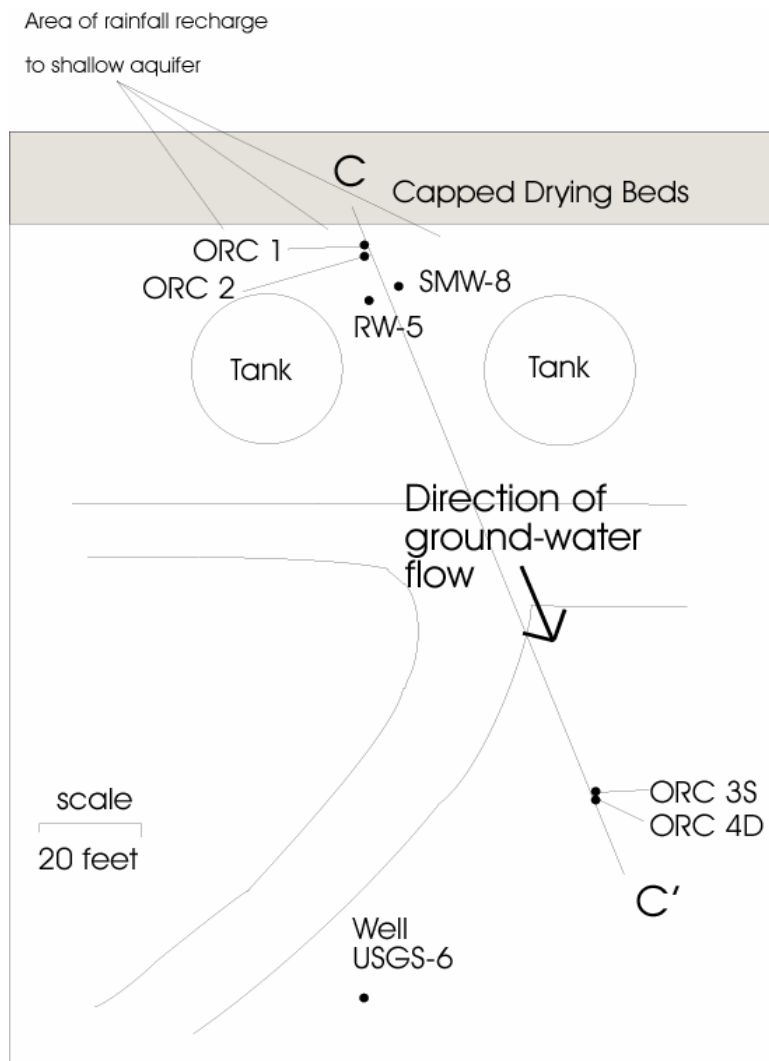
Figure 2. Map showing location of wells defining flowpath C-C' and the location of recharge to the shallow aquifer. (Source: U.S. Geological Survey, 1999. Natural Attenuation of Chlorinated Ethenes and Chlorinated Benzenes, Wastewater Treatment Plant, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina).

After the ORC® injection, concentrations of both benzene and chlorobenzene were lowered substantially in wells ORC-1 and ORC-2. In well ORC-1, which was nearest to the first line of ORC® injection, oxygen concentrations increased soon after injection, and concentrations of benzene and chlorobenzene decreased dramatically. Concentrations of oxygen, benzene, and chlorobenzene at well SMW-8, which is eighteen feet downgradient of the ORC® injection line, show a delayed effect caused by the transport time of ground-water flowing through the ORC® line. For the first two months there was no measurable effect on concentrations of dissolved oxygen. By September, 2001, concentrations of oxygen increased, and concentrations of benzene and chlorobenzene decreased. Contaminant concentrations remained low until the

oxygen-releasing capacity of the ORC® was exhausted, and then contaminant concentrations again increased. However, for the time period between September, 2001 and 2002, the ORC® acted as a contaminant source-area removal operation. Ground-water chemistry data collected during this time period was selected to test the NAS software for a source area-removal action.

In 2003, rising concentrations of benzene and chlorobenzene observed in well SMW-8 resulted in an investigation of the source of the contaminants. The sediments underlying the capped drying beds were sampled with direct-push technology in a grid pattern designed to locate any "hotspots", ground-water samples collected, and immediately analyzed by gas chromatography. The results of this investigation are shown in Figure 3, and they delineated a discrete hotspot of chlorobenzene contaminants adjacent to wells ORC-1, ORC-2, and SMW-8. A closer view of the hotspot in relation to wells ORC-1 and SMW-8 are shown in Figure 4.
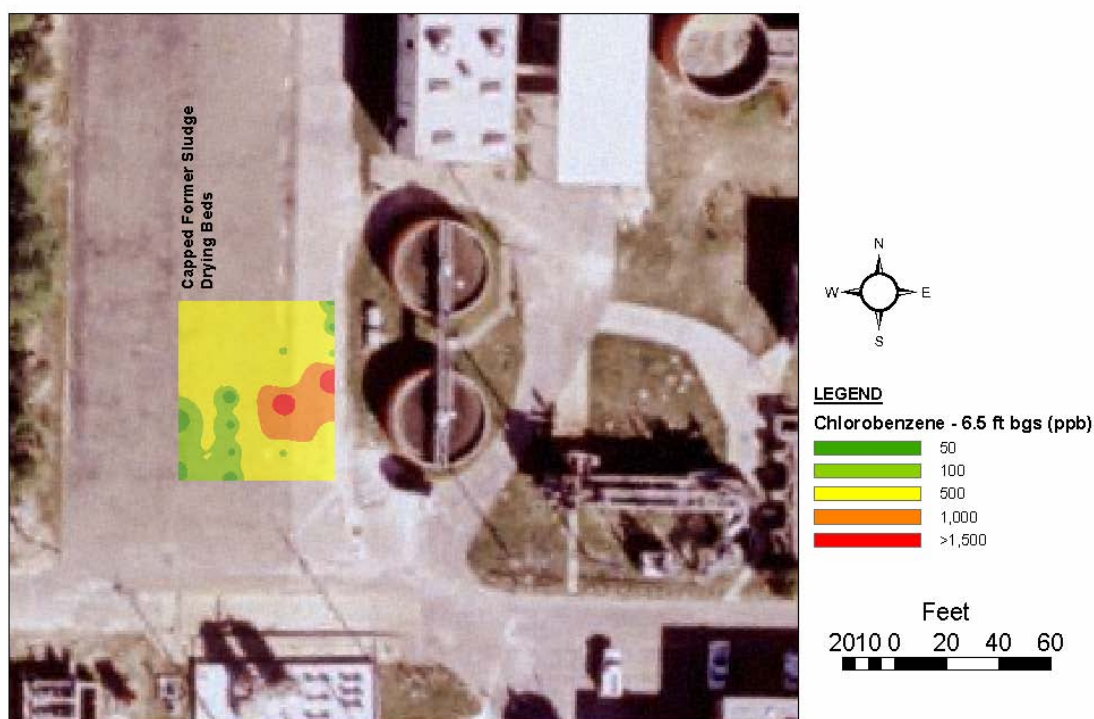
Contour of Chlorobenzene Concentrations at 6.5 Ft. Bgs (concentration in ppb).

Figure 3. Delineation of chlorobenzene hotspot underlying the capped former drying beds. (Source: U.S. Geological Survey, 2000. Delineation of a Benzene/Chlorobenzene Hotspot Related to Sludge Drying Beds at the WWTP, NAS Pensacola, U.S. Geological Survey, Columbia, South Carolina).
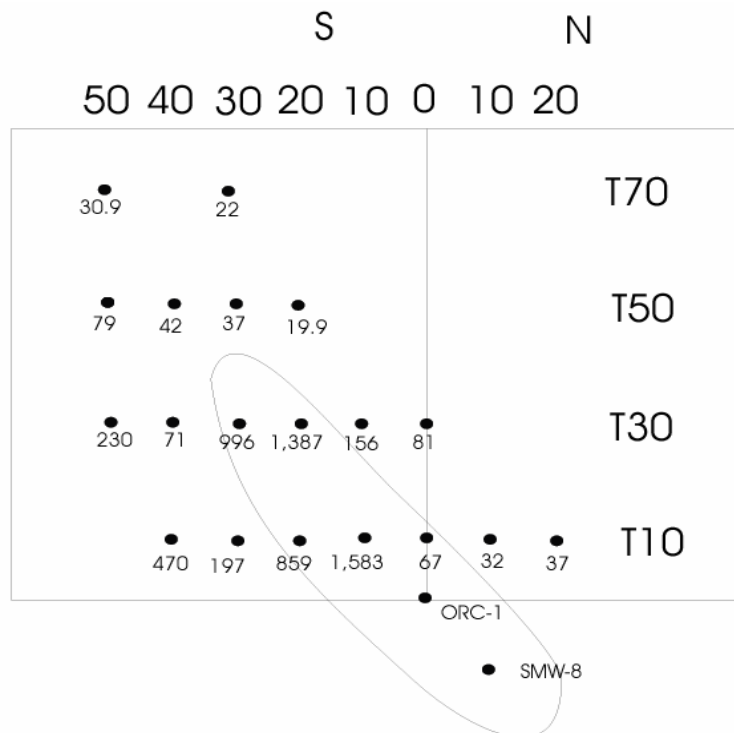
Figure 4. Concentrations of chlorobenzene @ 6.5 ft. below land surface and locations of wells ORC-1 and SMW-8.
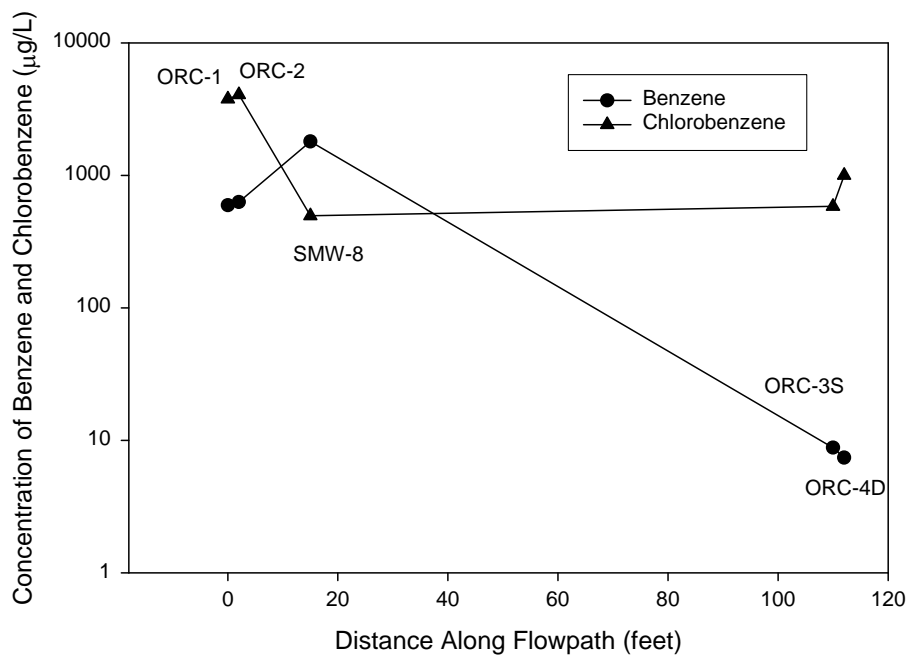
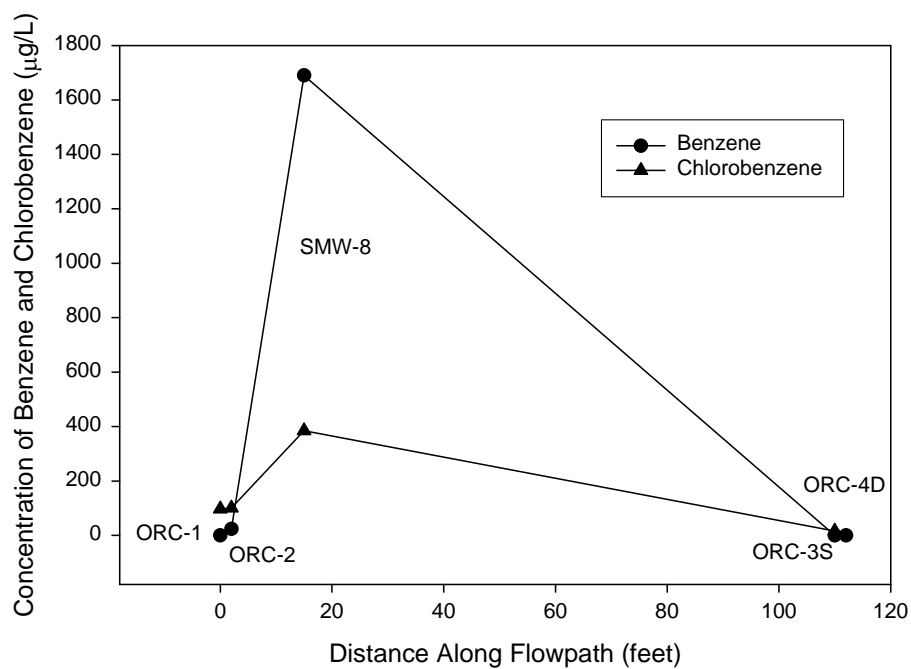**Figure 5. Concentrations of benzene and chlorobenzene along flowpath C-C' prior to ORC treatment.**

Figure 6. Concentrations of benzene and chlorobenzene along flowpath C-C' prior to ORC treatment.

2.3   Past and Current Remediation Strategies

As part of the RCRA response, large volumes of contaminated sediments and soils were removed from the abandoned sludge drying beds (EnSafe/Allen & Hoshall, 1997). The sludge drying beds and associated material were removed to a depth of six feet below land surface and disposed of as hazardous waste. The site was backfilled with clean sand, and capped with high-density asphalt. As part of these closures, a ground water-recovery system was put in place to pump and treat contaminated ground water.

3.0   Demonstration Approach

3.1   Modeling Objective

Two components of the NAS software were tested using site data collected at the WWTP. The first was the application of NAS to chlorinated benzenes including benzene, chlorobenzene 1,2-dichlorobenzene, 1,3-dichlrobenzene, and 1,4-dichlorobenzene. Because there was a "source area removal" action (the ORC$^{®}$ injection of 2001) undertaken that lowered contaminant concentrations at the source area below detectable levels, and because a monitoring well (SMW-8) is available to observed the effects of the "treated" water moving downgradient, the site is suitable for simulation using the DOS/TOS capability of NAS. In addition, because the actual NAPL source area has been delineated (Fig. 2), it is feasible to apply the NAPL dissolution features of NAS, including the pump-and-treat option, as well.

3.2   Input Parameters

The hydrologic and geochemical input parameters for the NAS simulations of the Pensacola WWTP are summarized in Table 1. Briefly, measured hydraulic conductivities at the site range from 42 to 38 ft/d, and measured hydraulic gradients range from 0.003 to 0.001 ft/ft. The effective porosity was estimated to be 0.3 on the basis of aquifer porosity. The NAPL source area was estimated to be 50 ft by 50 ft (Fig. 3), and was considered to be a mixture of benzene, chlorobenzene, and three different dichlorobenzene isomers. The aquifer contains very low concentrations of organic matter (~0.1%), and the predominant redox condition is Fe(III) reduction.

Table 1. Input Parameters for NAS Simulations of the Pensacola WWTP

Hydrogeologic Data and Contaminant Transport Calculations

	Maximum	Average	Minimum
Hydr. Conductivity [ft/d]	43	40	38
Hydraulic Gradient [ft/ft]	0.003	0.002	0.001
Total Porosity [-]		0.3	
Effective Porosity [-]		0.3	
Groundwater Vel. [ft/d]	0.43	0.267	0.127

Contaminant Source Specifications

Source Component	Conc Profile	NAPL Constituent
Total CBs	TRUE	TRUE
13DCB	TRUE	TRUE
12DCB	TRUE	TRUE
14DCB	TRUE	TRUE
CB	TRUE	TRUE
Benzene	TRUE	TRUE

Dispersion Parameters

Estimated Plume Length [ft]	743.4
Longitudinal Dispersivity [ft]	21.54
Dispersivity Ratio [-]	20
Transverse Dispersivity [ft]	1.08

Sorption Parameters
Fraction Org. Carbon [-]

Maximum	0.001
Average	0.001
Minimum	0.001

4.0 Performance Assessment

Time of remediation following source-area treatment

Concentrations of total chlorinated benzenes over time in ground water produced from Well SMW-8 following source area treatment (ORC) in 2001 are shown in Figure 5. In general, the observed data fall within the uncertainty envelope of the predicted time of remediation curves.

However, considerable variability between prediction and observation are evident. Similar comparisons between predicted and observed concentration trends are found with other contaminants as well.
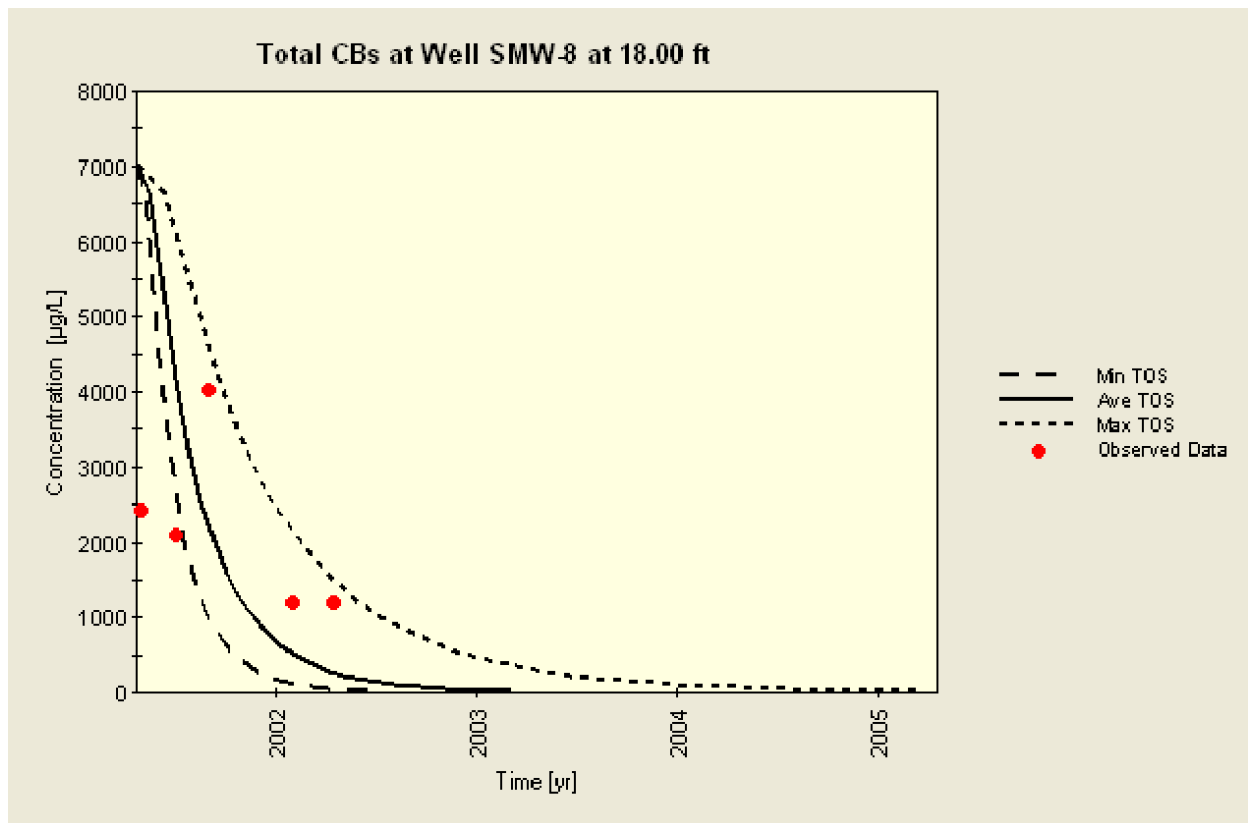

Figure 7. Concentrations of total chlorinated benzenes (CBs) over time at well SMW-8 following ORC treatment of the source area.
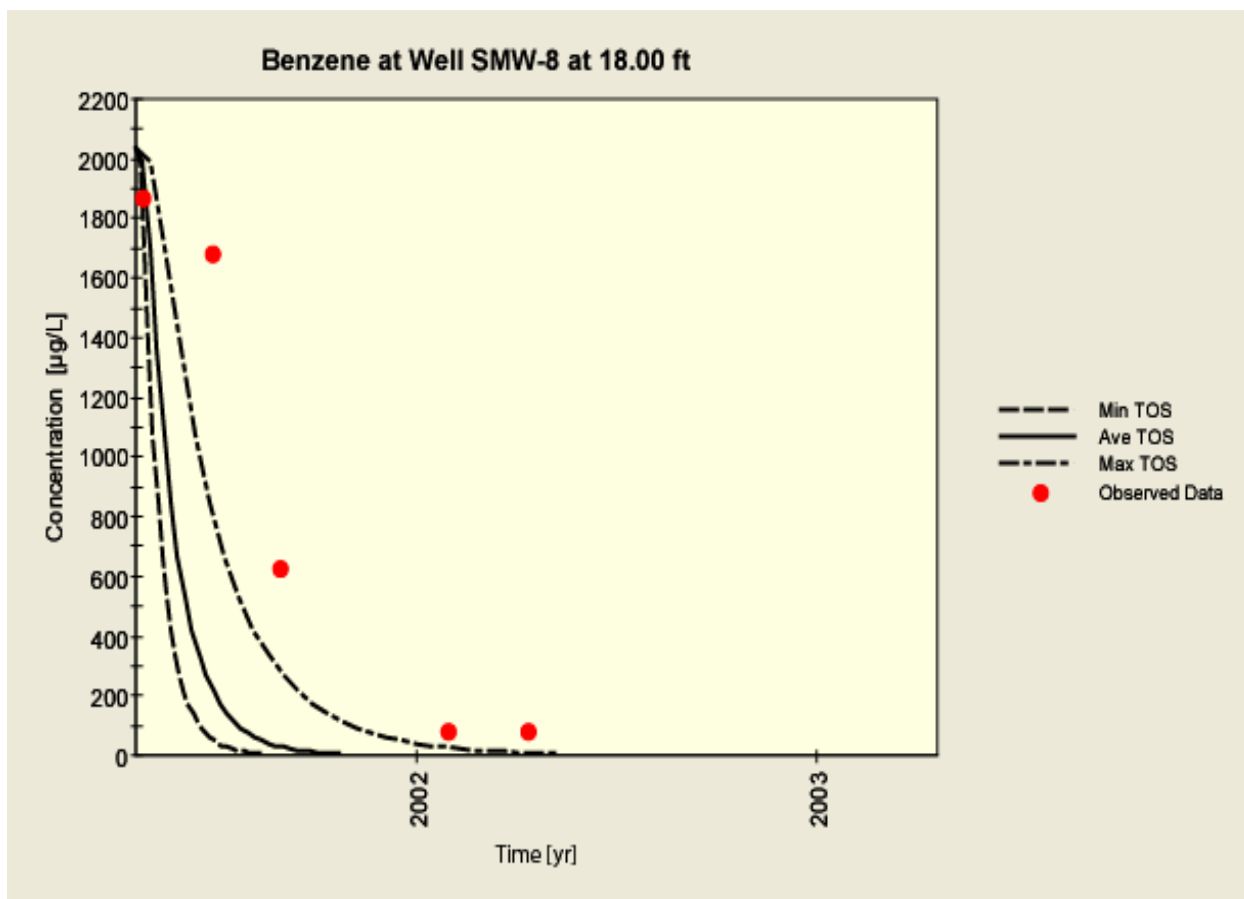
Figure 8. Concentrations of benzene over time at well SMW-8 following ORC treatment of the source area.

A comparison of predicted and observed benzene concentrations is shown in Figure 6. The concentration vs. time plot of benzene shows a different pattern than observed for total chlorinated benzenes. In particular, the observed data decrease systematically slower than indicated by the simulation. Concentrations of 1-3 dichlorobenzene in well SMW-8 (Fig. 9), on the other hand, show a rate of decrease greater than indicated by the NAS simulation.

Figure 9. Concentrations of 1-3 dichlorobenzene over time at well SMW-8 following ORC treatment of the source area.

Time of remediation using pump-and-treat
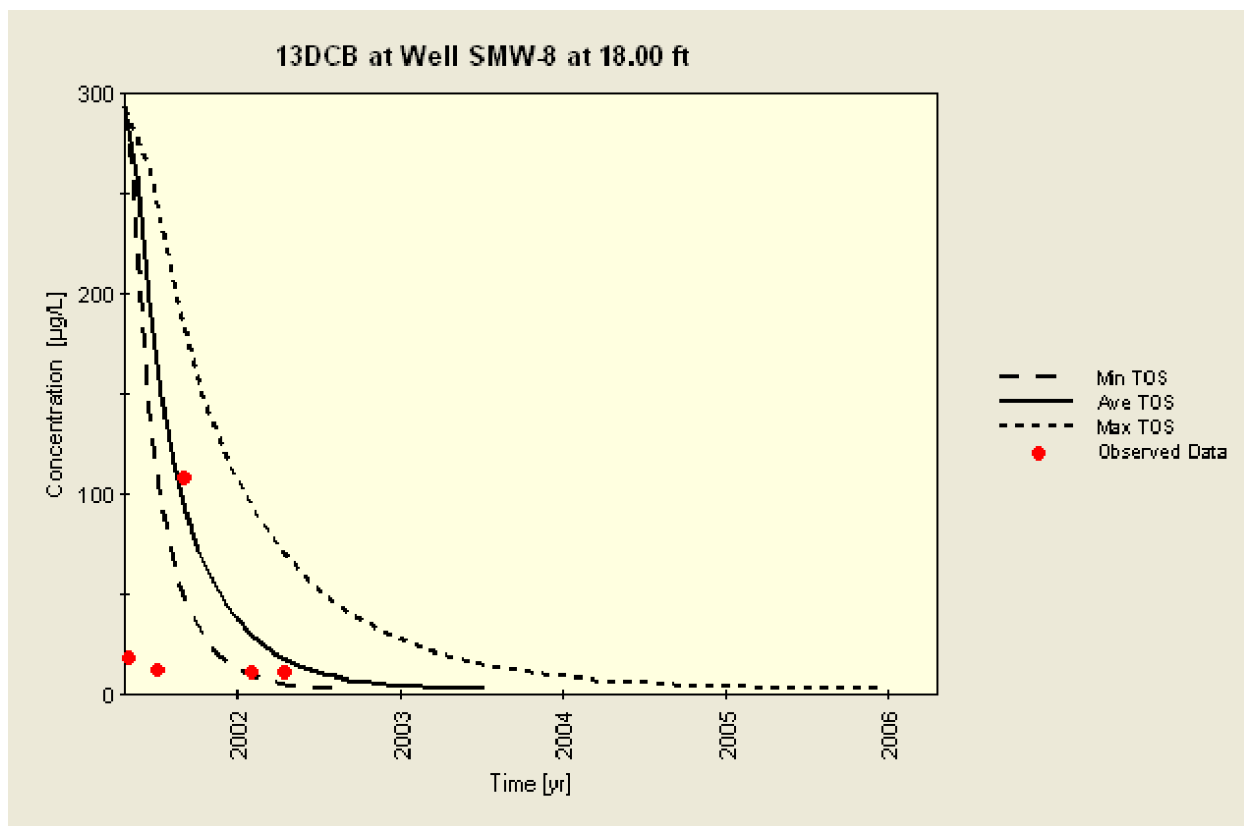
During the history of site operations, a pump-and-treat system was operated intermittently. One of the pumping wells was located approximately 40 downgradient of the contaminant source area. The pump-and-treat system was discontinued in 1999 because it was judged to be ineffective for either capturing the contaminant plumes or for lowering the time of remediation. Given the delineation of the source-area, and given NAS's capability to simulate pump-and-treat scenarios, those judgments can be reevaluated using NAS.

Table 2 shows times of remediation for the chlorobenzene source area assuming MNA only, as well as with pump-and-treat with an average pumping rate of 0.8 gal/min. In addition, a comparison of TOR for MNA versus pump-and-treat is shown in Fig. 10.

Table 2. Times of remediation associated with MNA and pump-and-treat.

	SCC [µg/L]	Mass [lb]	Removal Plan No Removal MNA	P&T
Total CBs	5.0	5,000	100+	98.8
13DCB	5.0	5,000	100+	65.0
12DCB	5.0	5,000	100+	93.9
14DCB	2.0	5,000	100+	81.0
CB	2.0	5,000	72.1	24.0
Benzene	2.0	5,000	6.0	3.8
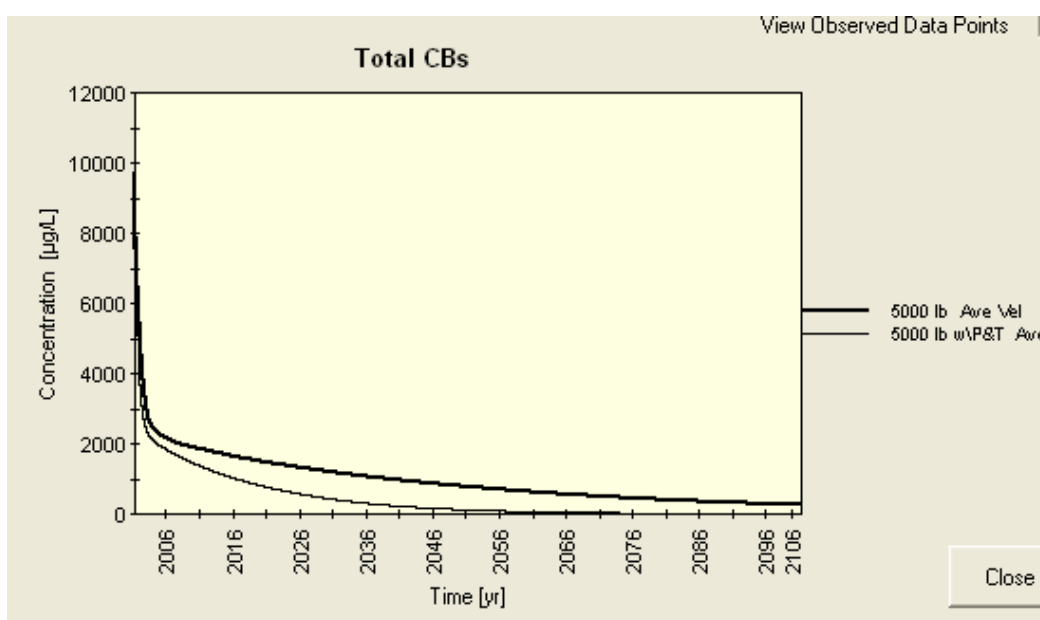
Figure 10. Comparison of TOR between MNA and pump-and-treat.

The results suggest that times of remediation for both MNA and pump-and-treat will be substantial. Furthermore, these simulations suggest that although pump-and-treat does lower times of remediation, they will remain large given the hydrologic constraints at the site. For these reasons, discontinuation of pump-and-treat and replacing it with source-area removal, as has been implemented at the site, is consistent with these NAS simulations.

Appendix H: Alaska DOT&PF – USGS (Peger Road) Site

Peger Road, Fairbanks, AK

1.0   Test Site

1.1   History of Operations at the Site

The Peger Road facility is operated by the Alaska Department of Transportation and Public Facilities (ADOT&PF), and has been used as an equipment maintenance and testing facility. A variety of solvents and petroleum hydrocarbons were used on site during the 1970s and 1980s. Release of these compounds has resulted in the formation of discrete TCE, PCE, and benzene plumes that have been characterized by the Alaska Department of Environmental Conservation (DEC) (Fig. 1).

Figure 1. Arial photo showing the Peger Road site and the extent of the TCE plume. (Source: Alaska Department of Environmental Conservation, 2005. ADOT&PF Peger Road Maintenance Facility, Fairbanks, Alaska).

1.2   Present Operation

The facility continues to be operated by the ADOT&PF, and the environmental contaminants are being monitored and managed by the Alaska DEC.

1.3   Selection of Site

Monitoring data for the TCE plume collected near the contaminant source area (well MW 98-10) are available from 1998 to 2004. In addition, DEC has installed numerous monitoring wells to delineate the areal extent of the plume. These data provide a record of source-area and plume contaminant concentrations over time. In addition, USGS personnel conducted an assessment of redox conditions (September, 2003), and performed laboratory studies to assess rates of TCE, DCE, and VC biodegradation rates under various conditions. This site provides an opportunity to compare NAS simulations of (1) TOS to long-term monitoring data, (2) TOR to long-term monitoring data, and (3) NAS-estimated rates of chloroethene biodegradation to laboratory-measured rates.

2.0   Site/Facility Characteristics

2.1   Hydrogeology

The Peger Road site is underlain by alluvial sediments deposited on the floodplain of the Chena River in the Fairbanks area. These sediments are characterized by relatively high hydraulic conductivities (200-600 ft/d) with a mean value of about 400 ft/d (USGS, 1998).

2.2   Source and Plume Description

TCE, PCE, and petroleum hydrocarbons were released prior to 1998 in several different locations (Fig. 1). A plume of TCE contamination, with it's has developed. Presently, the plume extends from the maintenance lab approximately to 19th Ave (Fig. 2). The soil zone overlying the TCE plume is characterized by permafrost, a feature which may affect vertical recharge to the aquifer. In addition, permafrost may locally affect directions of ground-water flow and thus the shape of the TCE plume (Alaska DEC, 2005). The aquifer is hydraulically connected to the nearby Chena and Tanana Rivers, and seasonal water-level fluctuations in these rivers affect hydraulic gradients in the aquifer. Rates of ground-water flow, therefore, also vary seasonally. For the purposes of NAS simulation, it is important to include observed variability in both hydraulic conductivity and hydraulic gradients.

2.3   Past and Current Remediation Strategies

Approximately 700 cubic yards of TCE-contaminated soil were excavated for the expansion of the Materials Laboratory on site. Excavated soil was land-spread to volatilize TCE.

2.4   Groundwater Flow and Transport Modeling – Previous work

A ground-water flow model simulating the interactions between the water-table aquifer and the nearby Chena and Tanana Rivers was developed by the U.S. Geological Survey to estimate the hydrologic properties of the aquifer.

Figure 2. Well location map for the Peger Road site. (Source: Alaska Department of Environmental Conservation, 2005. ADOT&PF Peger Road Maintenance Facility, Fairbanks, Alaska).

3.0   Demonstration Approach

3.1   Modeling Objective

The Peger Road sites provides an opportunity to compare NAS simulations of (1) time of stabilization (TOS) near the TCE source area to monitoring data (well MW98-10) collected over a six-year period. Similarly, the nature of site operations suggests the mass of TCE released over time was fairly small (less than 1000 lbs), and that the overall time of remediation (TOR) should be constrained by simulations of NAPL dissolution.

3.2   Input Parameters

3.2.1   Hydrogeologic Data

The range of hydrogeologic data used in the NAS simulations is tabulated in Table 1.

Table 1.—Hydrologic parameters used in NAS simulations

Facility Name:	Peger Road				Length:	feet
Site Name:	Fairbanks, Alaska				Time:	days
Additional Description:	TCE diffuse spill				Mass:	pounds

Hydrogeologic Data and Contaminant Transport Parameters

	Maximum	Average	Minimum			NAPL Source
Hydr. Conductivity [ft/d]	600.0	400.0	200.0	NAPL Source Length [ft]		50.0
Hydraulic Gradient [ft/ft]	0.002	0.001	0.0005	NAPL Source Width [ft]		100.0
Total Porosity [-]		0.3		Contaminated Aquifer Thickness [ft]		0.1
Effective Porosity [-]		0.3				
Groundwater Vel. [ft/d]	4.0	1.333	0.333			

Dispersion Parameters

Estimated Plume Length [ft]	1063.8
Longitudinal Dispersivity [ft]	25.13
Dispersivity Ratio [-]	20.0
Transverse Dispersivity [ft]	1.26

Sorption Parameters

Fraction Org. Carbon [-]

Maximum	0.005
Average	0.005
Minimum	0.005

	Total Chl. Eth.	TCE
Koc [L/kg]	126	126

Retardation Factor [-]

	Total Chl. Eth.	TCE
Maximum	4.9	4.9
Average	4.9	4.9
Minimum	4.9	4.9

The ground-water chemistry data used to assess the attenuation of TCE along the centerline of the plume and the redox characteristics of the system are shown in Table 2.

Table 2. Ground-water chemistry data used in NAS simulations of the Peger Road site.

Contaminant Concentration Profile (9/1/1998)

Well Name	Distance [ft]	Total Chl. Eth. [µg/L]	TCE [µg/L]
MW98-10	0	2370.	2370.
MW98-17	140	1100.	1100.
202A	360	120.	120.
N7A	780	9.	9.

Redox Indicator Concentrations (9/16/2003)

Well Name	Distance [ft]	Oxygen [mg/L]	Iron(II) [mg/L]	Sulfate [mg/L]	Redox Condition
MW98-10	0	3.	0.02	40.	Oxic
MW98-17	140	2.	3.4	85.	Oxic
202A	360	BD	13.	20.	Ferrogenic
N7A	780	BD	21.	26.	Ferrogenic

3.2.2 Source Characteristics

The source area was assumed to be approximated 100 feet wide and 50 feet long. The thickness of the NAPL-contaminated source area was varied during simulation from 10 to 0.1 feet.

3.2.3 NAC Analysis – Plume centerline concentrations and redox zonation

Concentrations of TCE and redox conditions along the centerline of the plume are shown in Figure 3. TCE concentration decreases indicate relatively low rates of biodegradation associated with oxic conditions near the source area, and continued low biodegradation rates in the Fe(III)-reducing conditions downgradient of the source area.

4.0   Performance Assessment

Simulation of C vs time without source-remediation

The results of NAS simulations of time of stabilization (TOS) at the nearest monitoring well downgradient of the source area (well MW98-17) are shown in Figure 4. As in all TOS simulations, the assumption is made that a source-area removal action has been undertaken (in this case, in 1998), and that a plume of remediate water is moving through the observation well. The simulated concentration profile curves represent the expected behavior of the plume for the

case of minimum, average, and maximum rates of ground-water flow. Also shown on Fig. 4 are the observed data points measured at the site.
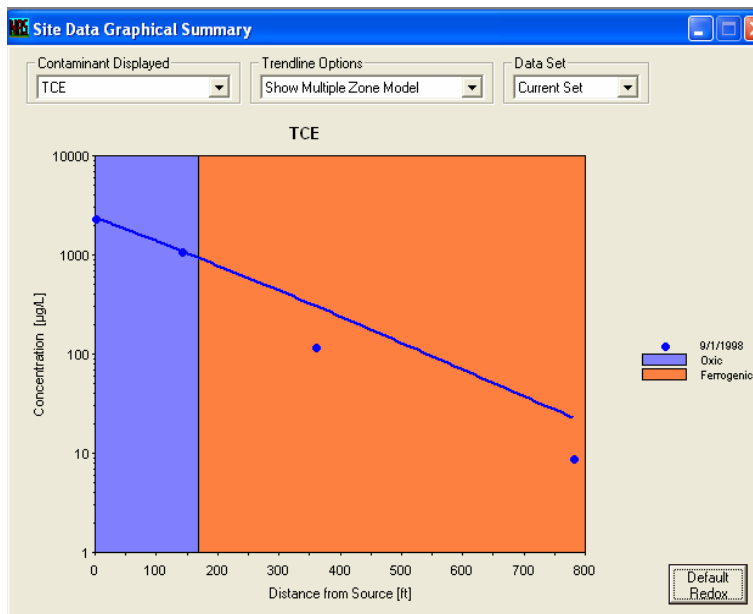

Figure 3. TCE concentration profile and redox conditions along the plume centerline. (Source: NAS snapshot).
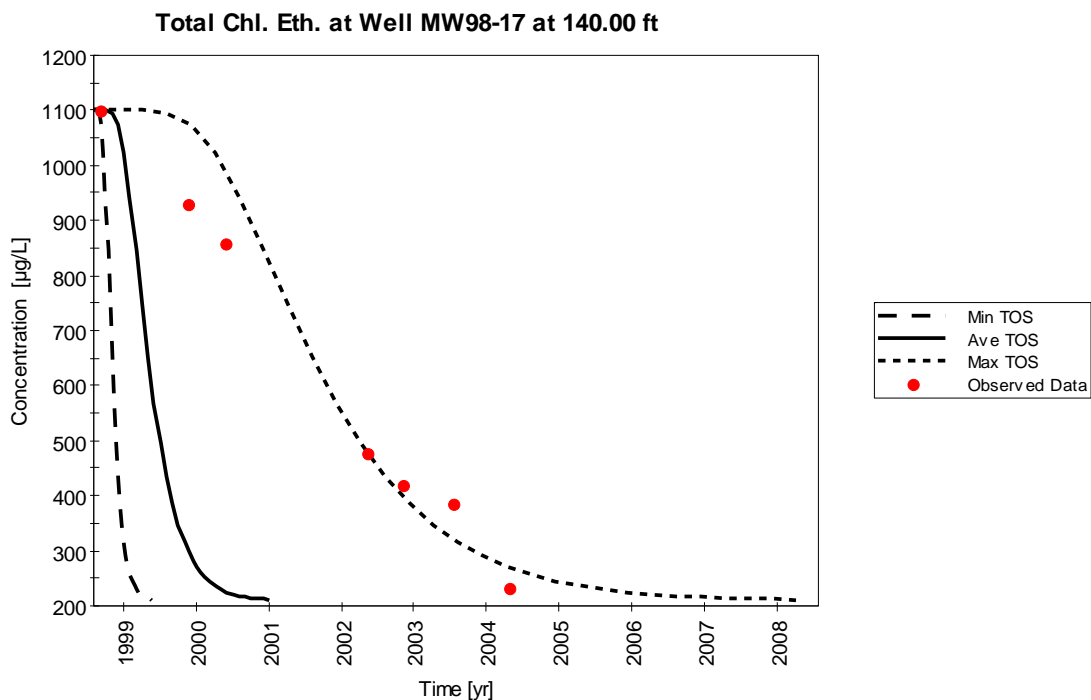

Figure 4. NAS simulation of time of stabilization at well MW98-17.

Inspection of Fig. 4 indicates that observed TCE concentrations at well MW98-10 clearly falls outside the envelope of uncertainty for maximum and minimum rates of ground-water flow. This behavior is expected because no source-area removal was undertaken in 1998 as assumed by the simulation. Interestingly, however, the overall shape of the observed TCE concentration decline is not dissimilar to the predicted behavior assuming the lowest rates of ground-water flow. One interpretation of these results is that (as expected) a source of TCE remains in or near the contaminant source area, but that this source is being depleted over time. Furthermore, this depletion is rapid enough that the observed behavior of the plume mimics a source-removal action. The next question to be address, therefore, is the nature of the apparent source-area depletion.

Simulation of C vs. time for NAPL dissolution

NAS simulation of NAPL dissolution and time of remediation (TOR) associated with the TCE source area of the Peger Road site is shown in Figure 5. The amount of TCE NAPL released at the site it not known. However, because the release is associated with solvents used to maintain vehicles at the site, it is likely that the mass of NAPL was fairly small and probably ranged between 100 and 1000 pounds. Furthermore, it is likely that NAPL was released over a period of years and contained components (such as petroleum hydrocarbons) in addition to TCE. The simulation shown in Fig. 5 assumes a NAPL mass of 500 pounds, that the mass fraction of TCE was 1%, that the NAPL is spread over an area of 100 by 50 feet, and that the thickness of the NAPL-contaminated zone is one foot. This results in an initial residual saturation for NAPL of 4.12×10^2. Furthermore, it was assumed that the NAPL was emplaced in the late 1980s.
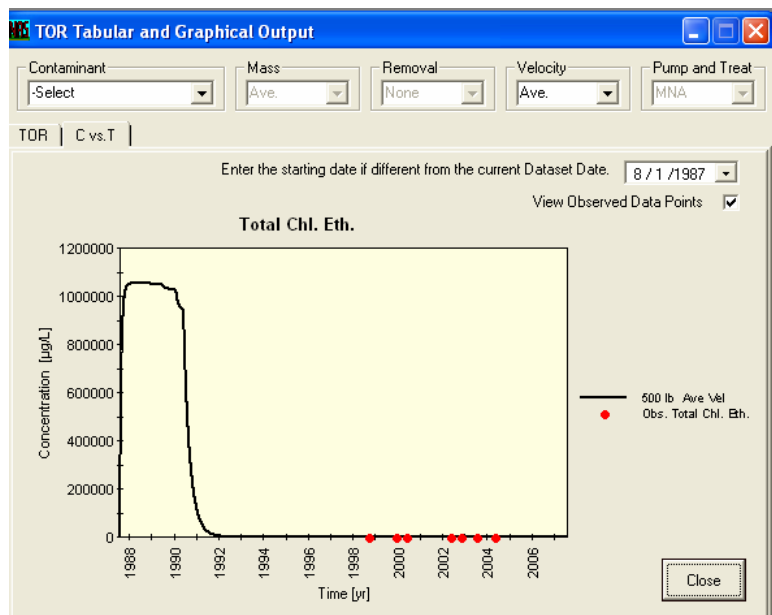

Figure 5. NAS simulation of NAPL dissolution at the Peger Road site.

The results of the simulation show that NAPL emplaced in the aquifer would be expected to dissolved fairly rapidly, even if the mass fraction of TCE in the NAPL is fairly low (1%). This expected behavior results from the relatively high hydraulic conductivity of the site and the high flux of ground water through the saturated zone. The observed TCE concentrations at well MW98-10 in the late 1990 are consistent with this expectation, and are much lower than they would be if a distinct NAPL phase were still present in the aquifer (Fig. 5). The TOR calculations for this scenario suggest that given a clean-up criteria of 2 µg/L downgradient of the source area, the time of remediation would be on the order of 6 to 7 years. This emphasizes the expectation that free-phase NAPL in this hydrologic environment would not be expected to persist for long periods of time, reflecting the rapid flux of ground water at the site.

These results appear to be at odds with the observation that concentration declines at well MW98-10 lag behind what would be expected if the source were removed (Fig. 4). A possible explanation of these results may be that, in the time period between 1980 and 2005, a significant pool of TCE remained in the soil zone, and that soil-zone TCE periodically (during the summer months) acted as a contaminant source. This would explain the "tailing" effect observed at well MW98-10. The Alaska DEC conducted a soil-removal operation at the site in 2005. If the soil was acting as a source of TCE in the time frame of available monitoring data, it would be expected that the rate of concentration declines at well MW98-10 will accelerate beginning in 2006. Continued monitoring of Well MW98-10 may shed light on this possibility.

Simulated and measured rates of TCE biodegradation

In 2003, the Alaska DEC initiated an experimental study of chloroethene biodegradation the Peger road site. Briefly, aquifer sediments from the site were collected, returned to the laboratory, and amended with several carbon-14 labeled chloroethene compounds, including TCE (Bradley and Chapelle, 2004). These experiments provide an opportunity to compare biodegradation rates estimated by NAS with laboratory-measured rates. The laboratory-derived rates were estimated in two ways. First, they were estimated by substrate loss (SL) of ^{14}C-TCE in the experimental vials over time. Secondly, they were estimated by daughter product production (DPP) of ^{14}C-TCE. Experiments were conducted with sediments collected from near the source are (well MW98-10), and in the downgradient part of the plume (well N4) (Figure 2). The results of this comparison are shown in Table 4.

The experimental rate constant measurement indicates very slow biodegradation in this system. These are some of the lowest TCE biodegradation rates measured in the laboratory, and are possible only because of the extreme sensitivity of the carbon-14 methodology used. The NAS-derived biodegradation rates are also very low, but they are consistently an order of magnitude higher than the laboratory-derived rate constants. The most appropriate conclusion that can be made from this comparison is that both methods indicate very low rates of TCE biodegradation in this system. The fact that the laboratory rates were lower than NAS-derived rates may or may not be meaningful. The NAS-derived rates reflect in situ conditions, and it is possible that sample handling and experimental manipulation decreased laboratory rates. Alternatively, the

hydrologic uncertainties associated with observation well data may artificially increase NAS-derived rates. In either case, both the experimental and NAS methods indicate low biodegradation rates at this site, which is consistent with the relatively oxidized nature of this system.

Table 4.—Comparison of experimentally-derived and NAS derived rate constants

Sediment (NAS redox zone)	Experimental Method	Experimental ^{14}C-TCE dechlorination rate (d^{-1})	NAS-derived TCE biodegradation rate (d^{-1})
MW 98-10 (aerobic zone)	SL	0.0001± 0.00015	Max 0.0247 Ave 0.0082 Min 0.0021
MW 98-10 (aerobic zone)	DPP	0.00015± 0.00006	
N3 (ferrogenic zone)	SL	0.00005± 0.00004	Max 0.026 Ave 0.0087 Min 0.0022
N3 (ferrogenic zone)	DPP	0.00015± 0.00008	